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SOLVENT SYSTEMS

R. V. Mertslin and V. D. Vasev

In his investigation of the solubility of various organic substances (acetotoluide, acetonaphthalide, phenylthiourea, benzoylphenylhydrazine, acetanilide, and benzamide) in ethyl alcohol – water mixtures at 25°, Antusch established the presence of a maximum on their solubility curves [1]. Subsequently, a similar case was discovered by Schreinemakers in the system: succinonitrile – water – ethyl alcohol, which he investigated in detail at 4.5° [2]. Herz and Knoch observed a similar phenomenon in the succinic acid – water – acetone and boric acid – water – acetone systems at 25° [3]. A.A.Grinberg [4] was the first to demonstrate the presence of a solubility maximum for a typical inorganic coordination compound – a tetrammineplatinitetrathiocyanoplatinate – in acetone–water and methanol–water mixtures. Subsequently, the existence of a maximum solubility of inorganic coordination compounds in mixed solvents was confirmed by other research workers [5].

Thus, we may consider it to be an experimentally established fact that there is such a thing as the increased solubility of certain substances – organic and inorganic, simple and complex – in mixed solvents. If we plot the solubility of the solid compcnent of these systems as a function of the solvent composition, we get a certain general geometrical picture that holds good for all such systems. Thus, in a square system, the basis of which is the line (A–B) representing the solvent composition, the verticals representing the corresponding solubilities of the given solid component, the solubility curve ($l_A m l_B$) will resemble the curve reproduced in Fig. 1. This curve shows that l_A and l_B, the solubilities in the individual solvents (A) and (B), increase as the solvents are mixed, and that the solubility curve possesses a flat maximum (m) located at a mixture whose composition is (X). It may happen that the values of l_A and l_B will be extremely small, i.e., that the given solid component will be practically insoluble in the individual liquid components, dissolving only in their mixtures. In view of this fact, it is well to call such mixtures of the liquid components solvent systems and to employ this term irrespective of the absolute values of l_A and l_B.

A.A.Grinberg was the first to attempt to provide a physical explanation for the foregoing phenomena; this is quite essential, inasmuch as thorough comprehension of this phenomenon is the only possible basis for solving the problem of the choice of solvents for any given concrete case. In his paper, A.A.Grinberg begins by calling attention to the physicochemical nature of a binary solvent system, pointing out, not without reason, that the relationship between its components might explain the increased solvent action of some mixtures as compared with the pure components. But, in analyzing this point of view, A.A.Grinberg strangely confined his attention to interactions that result in the formation of an undis-

sociated chemical compound. It is not surprising, therefore, that he encountered such difficulties as to force him to abandon an exploration of the problem from this point of view. Indeed, neither in the methanol–water system nor in the acetone–water system, both of which exhibit the phenomenon in question, can the presence of definite hydrates be proved, the formation of which might contribute to an explanation of the increased solubility of the solid component. Moreover, as A.A.Grinberg noted, such an explanation would contradict the research results of N.I.Stepanov [6], who demonstrated that systems in which interaction occurs possess a solubility minimum. All this compelled A.A.Grinberg to reject this manner of considering the problem.

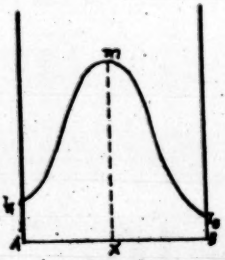

Fig. 1.

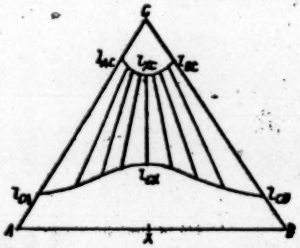

Fig. 2.

Abandoning the possibility of finding an explanation in the physico-chemical nature of the solvent systems, A.A.Grinberg turned to another concept, in which the increased solubility is related to the polar nature of the dissolved solid component, which is acted upon by the mixed solvent. Its low solubility in the individual liquid components is due to the solvation of only one part of the polar molecule, whereas both parts are solvated in solvent mixtures, resulting in an increase in solubility. It is worthy of note in this connection that A.A.Grinberg points out that "the molecular state of the solvent must play a considerable role" in this process, that "an associated solvent will be a weaker solvating agent than a depolymerized one." Unfortunately, the author limits himself to these expressions with regard to the physico-chemical state of the solvents, forgetting that in solvent mixtures this state might be very different from the individual states, particularly as far as the degree of association is concerned.

It is readily seen that whereas the first concept stressed chemical interaction between the solvents, the emphasis in the second concept is transferred to the interaction between the dissolved solid component and the liquid solvents, to the possibility of increased solvation in solvent mixtures. As for interactions among solvents and their effect upon an increased solubility, they are completely ignored, although the author of the concept considers the molecular state of the individual liquid components to be of undoubted importance for the phenomenon in question.

It seems to us that these problems will be correctly solved only when we are able to make allowance – in a case involving a maximum solubility of a solid component in a mixture of two liquid components – for the interaction of the latter two with each other as well as for their interaction with the dissolved object, in mixtures, that is, and not in their individual states. This complicated task naturally divides into two simpler ones, each of which underlay the two concepts of Grinberg's we spoke of earlier. Contrary to what Grinberg said, it seemed to us that we could achieve some measure of success by solving the first of

these problems, namely ascertaining the physicochemical nature of the solvent mixture that is able, under certain supplementary conditions, to exhibit increased solvent action over that of the individual solvents. It seems to us that the second problem, involving the determination of the physicochemical nature of the dissolved solid component that can exhibit an increased solubility in the given solvent mixture, is more difficult in the present state of our knowledge, notwithstanding the enticing simplicity with which Grinberg posed it in his second concept.

Thus, we shall turn to an elucidation of the physicochemical nature of those binary liquid systems that can exhibit an increased solvent action with respect to a suitable solid component. With this in mind, we point out that the crystallization of certain ternary systems must inevitably result in the formation of a solubility line of the kind we need. There is no doubt that systems of that type include ternary systems with two binary layers, but possessing two independent layering regions that intersect when the temperature is lowered, giving rise to a single layering region with a rational (singular or nonsingular) or an irrational maximum on the mutual solubility of the liquid phases, provided the same common component crystallizes in both ternary eutectics. We shall demonstrate that this assertion is correct. Let a ternary system ABC possess an isotherm of the mutual solubility of the liquid phases corresponding to the one shown in Fig. 2 at some temperature that exceeds the melting point of the more infusible component (C). It has only one layering region $l_{CA}l_{AC}l_{BC}l_{CB}$, with a maximum mutual solubility of the liquid phases located at the cross section CX. The layering region is covered with binodal tie-lines, in accordance with existing experience, the tie-line corresponding to the maximum having zero slope, i.e., lying on the cross section CX, whereas the tie-lines of the $l_{CA}l_{AC}l_{XC}l_{CX}$ area slope to the left, and the tie-lines of the $l_{CB}l_{BC}l_{XC}l_{CX}$ area slope to the right. Inasmuch as the system (AB) is the only homogeneously mapped one, it will predominate. Now let us lower the temperature, on the assumption that the layering region retains its qualitative characteristics, which does not exclude the possibility that its maximum will shift somewhat. A crystallization area of component (C) will appear when we get below the latter's melting point, this area subsequently approaching the points l_{AC} and l_{BC}. When these points are attained individually, a ternary eutectic begins to crystallize out, from the binary system (AC) as well as from the system (BC). One of the possible isotherms is represented qualitatively in Fig. 3. In this figure two ternary eutectic triangles $l_{CY}C_{l_Y}{}_{\cdot C}$ and $l_{CZ}C_{l_Z}{}_{\cdot C}$ are shown (in solid black for the sake of clearness), the tie-line sides of which enclose the layering region $l_{CY}l_{Y}{}_{\cdot}C_{l_X}C_{l_Z}{}_{\cdot}l_{CZ}l_{CX}$. Their rear sides $C_{l_{CY}}$ and $C_{l_{CZ}}$ abut on the regions of diphase equilibrium of the component (C) crystals and the solutions that are saturated with these crystals, which are situated along the lines $l_{S_CA}l_{CY}$ and $l_{S_CB}l_{CZ}$; these areas are indicated by the tie-lines. At the bottom of Fig. 3, these lines define the areas $l_{CA}l_{CY}l_{Y}{}_{\cdot}C_{l_{AC}}$ and $l_{CB}l_{CZ}l_{Z}{}_{\cdot}C_{l_{BC}}$ by binodal curves, these being labile areas and hence retaining their geometrical character, indicating an increase in the solubility of component (C) as we pass from solutions l_{S_CA} and l_{S_CB} to solutions l_{CY} and l_{CZ}, respectively. Lastly, a third region of diphase equilibria of the component (C) crystals with the solutions that are saturated with these crystals will lie between the sides $C_{l_Y}{}_{\cdot C}$ and $C_{l_Z}{}_{\cdot C}$ of the ternary eutectic triangles. These solutions lie along the line $l_{Y}{}_{\cdot}C_{l_{S_CX}}l_{Z}{}_{\cdot C}$ and the region will have a much higher concentration of component (C) than the preceding two. The homogeneous-state area $l_{Y}{}_{\cdot}C_{l_X}C_{l_Z}{}_{\cdot}l_{CS_CX}$ is situated between this region and that in which the two liquid phases are in equilibrium. Lowering the temperature still further causes the ternary eutectic triangles to approach still closer until they merge along the tie-line $l_{CX}l_{XC}C$ with zero slope (Fig. 4), the region of the diphase liquid state vanishing entirely in accordance with the reaction $l_{XC} \longrightarrow l_{CX} + S_C$. All that is now left of the isotherm is the line $l_{S_CA}l_{CX}l_{S_CB}$ of saturated solutions, with a

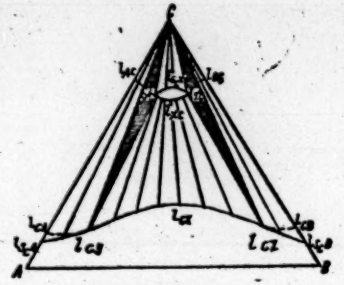

Fig. 3.

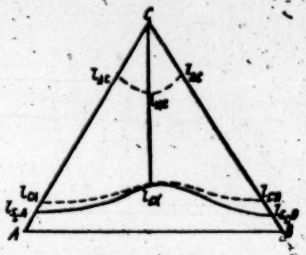

Fig. 4.

maximum at the point l_{CX}. Inasmuch as the labile layering region with a maximum mutual solubility of the liquid phases is conserved (dashed line in Fig. 4), the line of saturated solutions cannot have a solubility maximum of the solid component (C) that coincides with a maximum point in the layering region.

We have thus demonstrated that the ternary systems we have chosen yield the desired result upon cooling. To be sure, this by no means signifies that there are no other systems that might yield a similar result, even though they may differ somewhat from the one we have discussed. Thus, the requirement that two separately existing layering regions must approach each other, which might be deduced from the example investigated by Schreinemakers, may be regarded as unessential. It may be supposed that in some instances it is enough to have only one layering region instead of two, and so forth. What mattered to us was establishing the certainty that a solubility curve exhibiting a maximum is formed when we cool ternary systems that possess a single layering region with a maximum mutual solubility of the liquid phases, since the possibility of selecting such systems has been demonstrated to some extent. For systems of this type are formed chiefly when the solvent system (AB) predominates, i.e., when the interrelationships between its components are more markedly manifested than in the two other mapped systems (A–C) and (B–C), these interrelationships being manifested either by the formation of a chemical compound into which the associated components break down, or, in the more general case, by the formation of an associated compound that breaks down into the components, which in turn are dissociated to it. In the ultimate stage of the decomposition of the chemical compound this last case will turn into a case of the mutual decomposition of two associated components when they are dissolved in each other. The first instance of this has been discovered by R.V.Mertslin [8] in the acetic anhydride–water–gasoline system, in which he was able to detect singular fins on the polytherm of the layering surface, situated at the acetic acid–gasoline cross section; this was corroborated by K. I.Mochalov [9] for the acetic anhydride–water–hydrogen sulfide system. It is readily seen that the predominating system in this case is a singular one in the classification proposed by Academician N.S.Kurnakov. The predominant systems in the second case are irrational, i.e., the flat solubility maximum of the liquid phases does not occur at a rational ratio of the solvent components, and may shift in the diagram with a change in the equilibrium parameters. A priori, systems formed by aliphatic alcohols and ethers, aliphatic amines and water, aliphatic alcohols and water, heterocyclic amines and water, acetone and water, and ketones and alcohols are systems of this sort. It is possible that this type also comprises some systems that exhibit a minimum on their viscosity isotherms.

It must be stressed once again, however, that far from all the substances chosen as third components are able to produce the equilibrium situations described

above. It is highly probable that only those substances that are capable of solvation with the disintegrated disassociated molecules of the solvent components, i.e., that satisfy the fundamental condition of Grinberg's second concept, can exhibit the phenomenon of increased solubility in this group of mixed solvents, but only provided that the interrelationships between these latter rather than the interrelationship of the third component with one of the other two, predominate throughout the temperature range investigated. It must also be borne in mind that temperature changes may produce rather marked changes in the interrelationships between the solvent components, evin going so far as the production of normal relationships, which may radically change the conditions required for producing a maximum on the solubility curve.

We have made a study of the equilibrium of the liquid and solid phases in the ethyl alcohol–ether–succinonitrile system, in which the predominant binary system is ethyl alcohol–ether, which is doubtless of the type we require, in order to test these views of ours experimentally. As a matter of fact, Schreinemakers' researches [10] have proved that in the liquid state succinonitrile forms layers with ether as well as with alcohol, which is an *a priori* indication of the predominant role of the ethyl alcohol–ether binary system, since the latter is homogeneous throughout its liquid state. An examination of the rather extensive literature on the physical properties of this binary system enabled us to assume that this irrational system probably comprises a chemical compound (or compounds) that decomposes, as well as the disassociated molecules of the components. This is evidenced by: the boiling point isobar, which is convex toward the composition axis; the vapor-pressure and refractive-index isotherms, which are concave toward the composition axis; the extremely flat minimum on the specific-conductivity and heat of mixing isotherms; and the extremely peculiar viscosity isotherms [8,11]. We used succinonitrile with a m.p. of 50°, ether collected in the 34–34.5° interval, and alcohol with a b.p. of 78° in making up the mixtures for the system in question. The principal method we used to study the layering region and the adjacent regions of other heterogeneous states was that of Alexeev, which was supplemented when necessary by the isothermal titration with alcohol or the respective mixtures of the nitrile and ether; in some cases ether-alcohol mixtures were titrated.

TABLE 1

Composition at Points on the Polytherm of the Binary System: Ethyl Alcohol–Succinonitrile. Per Cent by Weight.

Test No.	Per cent of succino-nitrile	Temperature			Remarks
		Of crystal-lization	Of layer-ing	Ternary eutectic	
1	86.8	19.0	–	–	The composition corresponding to the end points on the line of triphase equilibrium, obtained by extrapolation, were as follows: 1) $C_2H_4Cy_2$ - 79.8, C_2H_5OH - 21.2; 2) $C_2H_4Cy_2$ - 13.0, C_2H_5OH - 87.0
2	78.7	11.5	–	–	
3	74.3	–	18.5	11.5	
4	68.2	–	24.5	11.5	
5	51.8	–	29.5	11.5	
6	39.9	–	30.0	11.5	
7	29.1	–	28.5	11.5	
8	19.7	–	23.5	11.5	
9	12.9	–	11.5	11.5	
10	10.0	6.0	–		

We first made a study of the binary mapping systems nitrile–alcohol and nitrile–ether. The results for the first of these systems are given in Table 1. We were able to find the composition of the terminal solutions (21.2 and 87.0% by weight of alcohol) by extrapolating the layering curve and the crystallization

curves along the ternary equilibrium line. Our results are in good agreement, on the whole, with those obtained by Schreinemakers in an older investigation of this system, especially for the solutions with a high percentage of alcohol; our polytherm for solutions poor in alcohol is somewhat lower in the diagram. The maximum discrepancy of some 2° between the polytherms occurs at the point of ternary equilibrium. There is not much difference between the critical temperatures, nor between the critical compositions, especially when we bear in mind the flat shape of the polytherms (our figures: 57% alcohol by weight and 30.5°C; Schreinemakers's figures: 59.2% alcohol by weight and 31.2°C).

The layering polytherm was not plotted for the other system to be mapped: water–ether, owing to the high homogenization temperatures. All we plotted was the line of ternary equilibrium at 29°, determining its terminal solutions: one with 17% by weight of ether, and the other with 96% by weight. The experimental data on this system are listed in Table 2.

TABLE 2

Composition at Points on the Polytherm of the System: Ether–Succinonitrile (Per cent by Weight)

Test No.	Per cent of succino-nitrile	Temperature: Of crystal-lization	Temperature: Of layering	Temperature: Ternary eutectic	Remarks
1	89.5	34.0	–	–	The composition corresponding to the end points on the line of triphase equilibrium, obtained by extrapolation, were as follows: 1) C_2H_4Cy = 83.0; $(C_2H_5)_2O$ = 17.0. 2) $C_2H_4Cy_2$ = 4.0; $(C_2H_5)_2O$ = 96.0
2	85.5	30.0	–	–	
3	82.0	–	34.5	29.0	
4	55.8	–	Not determined	29.0	
5	20.3	–		29.0	
6	14.6	–		29.0	
7	10.0	–		29.0	
8	5.2	–		29.0	
9	4.0	28.5	–	–	
10	2.5	17.0	–	–	

TABLE 3

Section at a Constant Alcohol–Ether Ratio of 79.8:20.2 (By Weight)

Test No.	Composition at the points (by weight): C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	Temperature: Crystal-lization	Temperature: layer-ing	Temperature: Ternary eutectic	Remarks
1	13.5	3.4	83.1	15.5	–	–	The composition corresponding to the end points on the line of triphase equilibrium, obtained by extrapolation, were as follows: 1) $C_2H_4Cy_2$, 72.0; C_2H_5OH, 22.3; $(C_2H_5)_2O$, 5.7. 2) $C_2H_4Cy_2$ – 19.0, C_2H_5OH – 64.6 $(C_2H_5)_2O$, 16.4
2	18.9	4.8	76.3	12.0	–	–	
3	24.3	6.1	69.6	–	16.5	10.8	
4	33.5	8.5	58.0	–	22.0	10.8	
5	41.7	10.5	47.8	–	23.0	10.8	
6	50.7	12.9	36.4	–	22.5	10.8	
7	58.3	14.7	27.0	–	20.0	10.8	
8	64.6	16.4	19.0	–	12.5	10.8	
9	66.2	16.8	17.0	9.5	–	–	
10	69.3	17.5	13.2	7.0	–	–	

The polythermal sections through the ternary system were passed through the nitrile vertex of the composition triangle and the points of the ether–alcohol binary system corresponding to 79.8%, 60%, 46%, 40%, 20%, and 10% of alcohol by weight. The resultant data are listed in Tables 3-8, respectively. It should be

TABLE 4

Section at a Constant Alcohol–Ether Ratio of 60:40 (By Weight)

Test No.	Composition at the points (by weight)			Temperature			Remarks
	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	Crystallization	Layering	Ternary eutectic	
1	9.8	6.5	83.7	20.0	–	–	The composition corresponding to the end points on the line of triphase equilibrium, obtained by extrapolation, were: 1) $C_2H_4Cy_2$, 69.5; C_2H_5OH 18.3; $(C_2H_5)_2O$ 12.2. 2) $C_2H_4Cy_2$, 21.5; C_2H_5OH 47.1 $(C_2H_5)_2O$, 31.4
2	13.6	9.1	77.3	13.5	–	–	
3	18.4	12.3	69.3	–	12.5	10.2	
4	24.2	16.2	59.6	–	18.0	10.2	
5	31.0	20.6	48.4	–	20.0	10.2	
6	39.1	26.1	34.8	–	19.0	10.2	
7	43.9	29.3	26.8	–	15.5	10.2	
8	47.9	31.9	20.2	9.8	–	–	
9	52.2	34.8	13.0	2.0	–	–	

TABLE 5

Section at a Constant Alcohol–Ether Ratio of 46:54 (By Weight)

Test No.	Composition at the points (by weight)			Temperature			Remarks
	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	Crystallization	Layering	Ternary eutectic	
1	10.3	12.2	77.5	17.0	–	–	Composition corresponding to end points on the line of triphase equilibrium, obtained by extrapolation, were: 1) C_2H_4Cy, 66.0; C_2H_5OH, 15.6; $(C_2H_5)_2O$, 18.4. 2) C_2H_4Cy, 21.6; C_2H_5OH, 36.1; $(C_2H_5)_2O$, 42.3.
2	15.2	17.8	67.0	10.5	–	–	
3	18.4	21.6	60.0	–	19.5	10.0	
4	23.0	27.0	50.0	–	21.5	10.0	
5	29.9	35.1	35.0	–	20.0	10.0	
6	33.6	39.4	27.0	–	16.0	10.0	
7	36.8	43.2	20.0	9.5	–	–	
8	40.0	47.0	13.0	3.0	–	–	

said that we determined only the first of these temperatures for all the sections, owing to the close proximity of the temperatures at the beginning and the end of ternary equilibrium in all the coordination compounds exhibiting this state. The isotherms for 10, 12, 15, and 20.5°, which are reproduced in Fig. 5 (a, b, c, and d), and the numerical data for which are listed in Table 9, were plotted from the polythermal sectional data. The practically linear shape of the ternary-equilibrium line for most of the sections, together with the slight differences in temperature of this state, both between the ends of a single section, as well as between adjacent sections, was a clear indication that the equilibrium situation changed sharply with the temperature, especially in the middle of the diagram and in solutions with a high percentage of alcohol. The plotting of the isotherms corroborated this conclusion, revealing a sharp change in the structural diagram with temperature.

Even a cursory inspection of the isotherms suffices to prove that they fully conform to the theoretical expectations expressed above. Thus, the 10° isotherm (Fig. 5a) clearly exhibits a solubility maximum of the nitrile in the alcohol–ether

TABLE 6

Section at a Constant Alcohol–Ether R tio of 40-60 (By Weight)

Test No.	Composition at the points (by weight)			Temperature			Remarks
	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	Crystal-lization	Layer-ing	Ternary eutectic	
1	8.2	12.2	79.6	21.4	–	–	The composition corresponding to the end points on the line of triphase equilibrium, obtained by extrapolation, were: 1) $C_2H_4Cy_2$, 69.0; C_2H_5OH, 12.4; $(C_2H_5)_2O$, 18.6 2) $C_2H_4Cy_2$, 23.5; C_2H_5OH, 30.6; $(C_2H_5)_2O$, 45.9.
2	11.6	17.3	71.1	13.0	–	–	
3	13.2	19.9	66.9	–	15.0	12.4	
4	19.0	28.4	52.6	–	21.5	12.1	
5	24.0	36.0	40.0	–	21.5	11.8	
6	24.9	37.4	37.7	–	21.0	11.8	
7	28.2	42.2	29.6	–	18.5	11.6	
8	30.4	45.5	24.1	–	13.0	11.5	
9	30.8	46.3	22.9	10.5	–	–	
10	32.1	48.2	19.7	9.5	–	–	
11	34.0	51.0	15.0	5.5	–	–	

TABLE 7

Section at a Constant Alcohol-Ether Ratio of 20:80 (By Weight)

Test No.	Composition of the points by weight			Temperature		Remarks
	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	Crystal-lization	Ternary eutectic	
1	4.5	17.8	77.7	19.0	–	Layering temperature was not determined in this section. The composition corresponding to the end points on the line of triphase equilibrium, obtained by extrapolation, were: 1) $C_2H_4Cy_2$, 79.0; C_2H_5OH, 4.2; $(C_2H_5)_2O$, 16.8. 2) $C_2H_4Cy_2$, 11.0; C_2H_5OH, 17.8; $(C_2H_5)_2O$, 71.2.
2	5.1	20.5	74.4	17.5	–	
3	7.1	28.3	64.6	–	15.8	
4	12.3	49.4	38.3	–	15.1	
5	15.0	60.0	25.0	–	14.8	
6	16.1	64.4	19.5	–	14.6	
7	17.3	69.4	13.3	–	14.5	
8	17.6	70.4	12.0	–	14.4	
9	18.0	72.0	10.0	10.5	–	
10	18.3	73.2	8.5	5.0	–	

mixture containing about 50% of the alcohol by weight (without the nitrile). The solubility curve gradually drops off on both sides of this composition. The heavy line in the figure denotes the tie-line existing at the lowest possible temperature, which is likewise the line of ternary equilibrium. The compositions of the two liquid phases entering into this equilibrium are shown on this line. Notwithstanding the absence of definite chemical compounds in the predominating binary liquid system, this ternary eutectic crystalizes at a constant temperature of 10°. At this temperature the ternary eutectic triangles, which approach each other from the sides representing the nitrile–ether and nitrile–alcohol binary systems, merge into a single straight line of zero slope. The terminal liquid phase of this ternary eutectic is situated at the maximum of the solubility curve.

Increasing the temperature by as little as 2 degrees causes a marked change in the state of the system. Now (cf the 12° isotherm in Fig. 5 b), the region of crystallization vanishes over a large area at the left. It is replaced by an area of two liquid phases, which is separated from the area of a homogeneous liquid state by lines that exhibit pronounced maxima and minima. Inasmuch as the selected temperature of 12° is 0.5° above the ternary euthectic point in the nitrile – alcohol system, the isotherm exhibits only one ternary eutectic triangle, which

TABLE 8

Section at a Constant Alcohol–Ether Ratio of 10:90 (By Weight)

Test No.	Composition of the points (by weight)			Temperature		Remarks
	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	Crystallization	Ternary eutectic	
1	2.3	21.1	76.6	23.0	–	Layering temperature was not determined in this section. The composition corresponding to the end points on the line of triphase equilibrium, were: 1) $C_2H_4Cy_2$, 71.0; C_2H_5OH, 2.9; $(C_2H_5)_2O$, 26.1. 2) $C_2H_4Cy_2$, 6.0; C_2H_5OH, 9.4; $(C_2H_5)_2O$, 84.6.
2	3.3	29.2	67.5	–	20.4	
3	4.5	40.3	55.2	–	20.2	
4	8.0	72.0	20.0	–	19.6	
5	8.5	76.0	15.5	–	19.6	
6	9.0	81.0	10.0	–	19.5	
7	9.3	83.5	7.2	–	19.4	
8	9.5	85.3	5.2	5.0	–	

TABLE 9

Composition at Points on the 10, 12, 15, and 20.5° Isotherms (Per cent by Weight)

Test No.	10°			12°			15°			20.5°		
	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$	C_2H_5OH	$(C_2H_5)_2O$	$C_2H_4Cy_2$
1	–	98.0	2.0	–	97.9	2.1	–	97.8	2.2	–	97.0	3.0
2	9.5	85.2	5.3	9.4	85.0	5.6	9.5	85.3	5.2	83.0	–	17.0
3	18.0	72.2	9.8	18.0	72.0	10.0	17.8	71.2	11.0	57.9	14.6	27.5
4	88.0	–	12.0	87.0	–	13.0	86.2	–	13.8	26.8	40.2	33.0
5	65.9	16.7	17.4	35.4	41.6	23.0	63.0	16.0	21.0	29.0	34.0	37.0
6	31.6	47.4	21.0	64.0	16.2	19.8	30.0	45.0	25.0	5.8	51.7	42.5
7	47.3	31.5	21.2	46.5	31.0	22.5	34.0	40.0	26.0	33.0	22.0	45.0
8	36.1	42.3	21.6	30.5	45.7	23.8	44.4	29.6	26.0	28.2	18.8	53.0
9	15.6	18.4	66.0	20.0	30.0	50.0	12.0	48.0	40.0	17.2	25.8	57.0
10				15.9	18.6	65.5	16.6	19.4	64.0	29.5	7.5	63.0
11				19.1	12.8	68.1	20.9	13.9	65.2	28.5	–	72.5
12				22.5	5.7	71.8	13.3	19.9	66.8	4.2	16.8	79.0
13				21.6	–	78.4	23.9	6.1	70.0	9.6	6.4	84.0
14				14.1	16.5	69.4	10.6	15.9	73.5	8.7	10.1	81.2
15				13.8	16.2	70.0	11.8	13.8	74.4	12.0	–	88.0
16				20.5	–	79.5	23.5	–	76.5	7.6	11.4	81.0
17				5.2	18.3	76.5	12.6	8.4	79.0	2.3	11.7	86.0
18				15.1	10.1	74.8	14.4	3.6	82.0			
19							17.0	–	83.0	4.4	17.6	78.0

divides the nitrile crystallization area into two parts, so that the solubility of the solid nitrile in alcohol–ether mixtures at this temperature cannot be expressed by a single continuous curve. In fact, starting with a saturated solution in ether, the solubility curve exhibits a rise in the solubility of the nitrile as the percentage of alcohol in the mixtures increases. This increase reaches a limit as soon as we reach the solution composition that constitutes the ternary eutectic. Any further increase in the percentage of alcohol now results in formation of a new saturated solution with a much higher percentage of the dissolved

nitrile. Thus, when ternary eutectic equilibrium is attained, there is a sharp rise in the solubility of the nitrile in the second liquid phase, which is the only one left, as a saturated solution, as the transition occurs to solvent mixtures with a still higher percentage of alcohol. The new solubility curve exhibits an uninterrupted rise in the nitrile solubility up to the maximum value attainable in the nitrile-alcohol binary system.

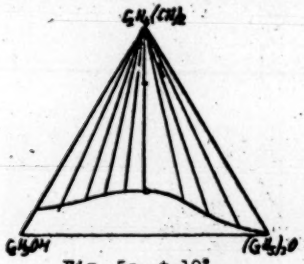

Fig. 5a. t 10°.

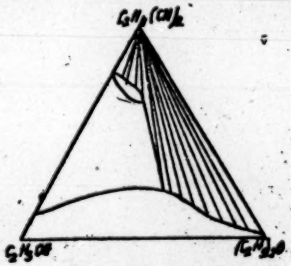

Fig. 5b. t 12°.

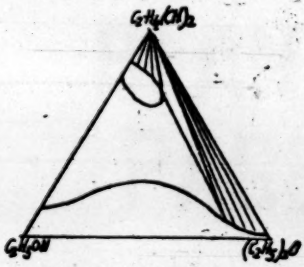

Fig. 5c. t 15°.

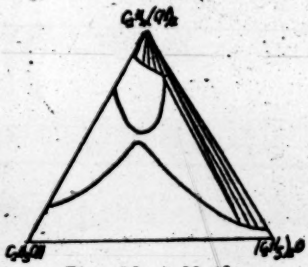

Fig. 5d. t 20.5°.

There is no need for a detailed description of the other isotherms, particularly, the 15° isotherm reproduced in Fig. 5 (Fig. 5c), since they all resemble the one just described, differing from it solely in the increased area of the region in which the two liquid phases are in equilibrium, the ternary eutectic triangle gradually, but steadily approaching the line of the nitrile-ether binary system. It is seen that this is paralleled by an approach of the maximum and minimum points of the liquid-phase solubility curves. Plotting the maximum temperature recorded in the region of diphase equilibrium along any of the sections drawn by us on the axis of ordinates, and plotting the percentage composition of the solvents on the axis of abscissas, we get the curve reproduced in Fig. 6. It is evident from this figure that the maximum temperature at which a single layering region exists is approximately 20.5°. Beginning at this temperature and at a section representing an alcohol-ether ratio of 52.5:47.5, the layering region splits into two parts, each having its own critical point. One of these will move over toward the nitrile-alcohol binary system as the temperature rises, the other moving over toward the nitrile-ether system. This isotherm is reprcduced in Fig. 5 d.

Let us now summarize the results of our investigations. We advanced the hypothesis that the maximum solubility of certain substances in mixed solvents is a function of the relationships between the latter and the dissolving substance.

Examination of a series of isotherms for the case under discussion, starting with the lowest temperatures, demonstrated with ease that the isotherm displaying a maximum solubility is genetically related to the isotherms that contain an area of diphase liquid equilibrium with a maximum solubility in the liquid phases. Since the latter exist only at a definite ratio of the solvent components and, moreover, only when these binary systems predominate, we are able to limit our choice of solvent systems in advance, thus facilitating the exploratory work considerably. At the present time we do not know what relationship must exist between the solvents and the dissolved solid for the latter to display a maximum solubility in mixed solvents, but nonetheless we can now state one criterion that is undoubtedly necessary. In fact, when such a ternary system is converted, at a high enough temperature into a system with limited solubility in the liquid phases, the area of which must be traversed by the lines of the abutting binary systems, we may conclude that the dissolved solid forms binary systems that exhibit layering with each of the solvents separately. It is very often practically impossible to reduce such systems to a state of ternary equilibrium (a ternary eutectic), because of the solvents' low boiling points, or because of the extremely high temperature at which the ternary equilibrium exists, or, lastly, because of the occurrence of an irreversible chemical transformation with the system. When this is so, it is useful to remember that binary systems that exhibit layering usually have a very small temperature coefficient of solution for the solid, so that the magnitude of the latter may enable one to estimate a priori whether the given binary system meets the required specification or not. If both of the solvents chosen prove to be suitable in this sense, we may expect to get an isotherm exhibiting maximum solubility, provided the two solvents are completely soluble in each other, constituting a binary systems that exhibits either mutual decomposition of the associated components or decomposition of the chemical compound they form into its constituents. Application of these principles to the ternary system formed by succinonitrile with ethyl alcohol and ethyl ether enabled us to demonstrate their correctness without difficulty, experimentally proving the existence of a solubility curve with a maximum for the solid nitrile at low temperatures, and the existence at high temperatures of an area of equilibrium of two liquid phases, bounded by curves that likewise exhibit maximum mutual solubility of these phases, and to prove the existence of a genetic bond between them.

Fig. 6.

SUMMARY

1. The assumption is put forward that in ternary systems consisting of two liquids and one solid, the solubility curve of the latter can have a maximum only when certain relationships exist between the liquid components. The necessary conditions are that this binary system be the predominating one and contain associated components that either decompose mutually or form a chemical compound that in turn decomposes in a solution of these components.

2. The fact that the isotherms of ternary systems exhibiting a maximum solubility of the solid component in mixtures of the two liquid components are related to isotherms that display a diphase liquid state with a maximum mutual solubility of the liquid phases has been proved theoretically.

3. The opinions expressed have been confirmed experimentally by the equilibria produced in a ternary system constituted by succinonitrile, ethyl alcohol, and ether.

4. Some exploratory criteria are laid down for solvent systems for a given solid.

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THE CORRELATION OF PROPERTIES IN THE METAL SERIES COPPER-SILVER-GOLD

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In contrast to the unvarying development of properties observed as we pass from one member to the next of many subgroups in the periodic system (such as, Na, K, Rb, and Cs; F, Cl, Br, I, etc.), the middle member of the subgroup referred to in the title – Ag – possesses extreme values of most properties.

We have listed similar properties for the corresponding members of two subgroups in Table 1, together with some important physical and mechanical properties, in an effort to disclose the reasons for this behavior.

We might point out that the divergence in the nature of the change of properties is observed principally when we pass from rubidium to cesium and from silver to gold; the changes in properties observed as we pass from potassium to rubidium and from copper to silver conforms on the whole to the general pattern of behavior. Nor is it hard to see that it is not silver, but rather gold, that occupies a special position among the elements we have compared. This distinction obviously involves the fact that the 4f subgroup is related to the genesis of the lanthanoids (Table 2).

The filling up of the 4f subgroup as the overall line of development of the genesis of the elements continues involves the existence of electrons in at least the 6s subgroup. The filling up of the inner subgroup, which is still fairly far from the nucleus, results in an increase in the influence of the nucleus upon the outer electrons, owing to the incomplete screening of the nucleus' charge by this subgroup. The outer electrons are drawn closer to the nucleus, as it were. This is, as we know, the reason for the lanthanoid contraction. This may likewise be regarded as the fundamental reason why the effective charge of the gold nucleus is higher than that of the silver nucleus, notwithstanding the higher principal quantum number of gold's outer electron. We define the effective charge of a nucleus as the positive charge that acts upon the valence electrons. Hence, the principal result of the presence of the lanthanoids in the series of the elements is an increase in the effective charge of the nucleus in elements with high atomic numbers.

More than a third of the chemical elements known to us exhibit the effect of the lanthanoid contraction. Research upon the effect of this upon the physical,

TABLE 1*

Property \ Metal	K	Cu	Rb	Ag	Cs	Au
Ionization potential, volts	4.32	7.69	4.159	7.54	3.877	9.25
Atomic radius, Å	2.32	1.276	2.54	1.442	2.74	1.44
Melting point, °C	63.65	1084	38.9	960.5	29.7	1063
Boiling point, °C	760	2560	707	2170	700	2950
Close-packing coefficient, $kg^{-1} \cdot cm^2$...	357	7.2	520	9.9	700	5.8
Atomic conductivity at the characteristic temperature, $ohm^{-1} \cdot 10^{-4}$	142	104	130	192	124	176
Coefficient of linear expansion X 10^6	84	16.4	90	18.7	97	14.2
Refractive index at λ = 5500 Å and color.....	0.05	0.9 red	0.14	0.2 white	0.32	0.6 yellow
Modulus of transverse elasticity X $10^4 kg/mm^2$.....		125		0.81		0.81
Ultimate tensile strength, kg/mm^2.....		22		13		14
Critical shearing stress, kg/mm^2.....		0.10		0.06		0.09

TABLE 2
Electronic Formula of the Normal State of Free Atoms

Element and atomic number	1	2		3			4				5		6	
	s	s	p	s	p	d	s	p	d	f	s	p	d	s
19 K	2	2	6	2	6	-	1							
29 Cu	2	2	6	2	6	10	1							
37 Rb	2	2	6	2	6	10	2	6	-	-	1			
47 Ag	2	2	6	2	6	10	2	6	10	-	1			
55 Cs	2	2	6	2	6	10	2	6	10	-	2	6	-	1
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10	1

chemical, and so-called engineering properties of substances is far from as extensive, however, as it merits. This effect may manifest itself differently upon various properties of various elements. This effect ought to be most clearly manifested (not being masked by complex electron interrelationships) in the first period of the periodic system. Not much is known of Element 87, so that the series: copper – silver – gold is probably best fitted for our purposes.

If there were no antiscreening action, the ionization potential ($Ke^0 \rightarrow Ke^+$) ought to drop as we pass to lower atomic numbers within the group, owing to an increase in the principal quantum number and a decrease in the linkage to the nucleus. The increase in the effective charge reinforces the linkage to the nucleus (or to the ionic framework), however, and makes the decrement of the ionization potential smaller as we travel down the group; this latter decrease may be so great as to make the decrement negative. That is precisely what happens in the

*After van Arkel, Reine Metalle, Berlin (1940) and Encyclopedia of the Physics of Metals Vol. 1 1937.

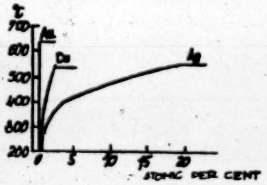
copper – silver – gold series: the ionization potential of gold is higher than that of silver.

Notwithstanding the rise in the principal quantum number, the increase in the effective charge of the gold nucleus results in a decrease in the decrement of the atomic radii, even making it somewhat negative (nor must it be forgotten that the increase in the nuclear charge is only 18 units between copper and silver, whereas it totals 32 units between silver and gold).

A decrease in the atomic radius (the configuration of the electronic fields remaining the same) results in an increase in the strength of the bond between the particles within the space lattice.

This must be reflected in gold having a higher melting point than silver, inasmuch as it has been repeatedly shown that the melting point is a fairly reliable index of the strength of homotypic crystal structures. All this is borne out by the data listed in the table.

The weaker forces existing in silver as well as the smaller potential gradient in the silver lattice, must result in an increase in the close-packing coefficient;* this is also confirmed by experimental data. The distinctive electron density of silver is also reflected in its color. Silver is a white metal, in contrast to copper and gold, which are colored. The "post-lanthanoid" position of gold is reflected in its mechanical properties, viz.: as far as its principal mechanical properties are concerned gold "returns" to the upper members of the subgroup.



The manifestation of the lanthanoid effect upon solubility phenomena is extremely interesting. In spite of the fact that the atomic radii of silver and gold are practically identical, in the solid state gold dissolves indefinitely in copper at high temperatures, whereas no more than 12 atomic per cent of silver dissolves. This phenomenon can also be explained from the point of view set forth above. As a result of the increase in the effective charge of the gold nucleus, the strength of the bond between the atoms of gold and copper approaches that in pure copper or in pure gold, whereas there is a greater difference between the strengths of the bonds in pure copper, between silver and copper atoms, and in pure silver, so that the entropy of a system consisting of two diphase solutions of low concentrations is higher than the entropy of a monophase system consisting of a mixture of two neighboring elements.

Let us consider still another example: the solubility of copper, silver, and gold in aluminum.

As we know, aluminum has the same type of space lattice as the other three metals, its parameter differing by less than 1% from the lattice parameter of silver or gold, but the internal field is much weaker in aluminum than in the series under discussion (the ionization potential of aluminum is 5.9 volts, and its melting point is 660°); correspondingly, the solubility of silver, as the "weakest" member of the series, is much higher than that of copper or gold. Gold is practically insoluble in aluminum (figure).

The extremely low solubility of all these metals as a group in aluminum, notwithstanding the favorable structural and volume factors, especially in the case of silver and gold, is also noteworthy. This is doubtless due to the different distribution of the electron densities – a difference in electron configuration – in aluminum as contrasted with the metal series in question.

*In our opinion the inner potential gradients play a major part in the compressibility process and in the deformation in general since they reflect the nature of the chemical bond between the points of the lattice.

SUMMARY

1. The uniformity of change of properties in the metal series: copper – silver – gold is violated in many instances in which the values of the gold properties "return" to the corresponding values for the upper members of the series.

2. This behavior of gold is due to the effect of lanthanoid contraction – the filling up of the 4f subgroup, resulting in an increase in the effective charge of the nucleus (or of the ion framework).

3. The increase in the effective nuclear charge of the post-lanthanoid elements must always be borne in mind in analyzing the relative properties within groups of the periodic system.

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THE PHYSICOCHEMICAL INVESTIGATION OF THE PHOSPHOROUS TRICHLORIDE - BROMINE SYSTEM. I

Ya. A. Fialkov and A. A. Kuzmenko

The chemical literature contains several papers devoted to a study of the higher halides of phosphorus, including mixed halides, i.e., those containing different halogen atoms. Many of these phosphorus halides are listed in Table 1, which gives the formulas and some of the properties of these compounds. The table covers the halides that contain more than 5 halogen atoms.

TABLE 1

Higher Halides of Phosphorus

Formula	Properties	References
PCl_3Br_4	Ruby red crystals that decompose at 60°.	[6,7]
PCl_2Br_5		[9]
PBr_7	Melting point 106°	[4]
PCl_6I	Orange-yellow crystals that do not melt, but sublime above 200°	[10]
PBr_6I	Cherry-red needles, m.p. 114.6°.	[11]
PCl_3Br_5	[illegible]	[6,7]
PCl_2Br_7		[6,7,9]
PBr_9	Melting point 106°	[4]
PCl_3Br_8	Brown crystals that melt at 25°, distils at 90° without decomposition	[5,7]
$PCl_5 \cdot 5Br_2$	Red-brown crystals that decompose at room temperature	[12]
PBr_{17}		[4]
PCl_3Br_{18}		[1,13]

As we see from Table 1, all the halides of phosphorus listed therein may be divided into several groups, according to the number of halogen atoms associated with one phosphorus atom: PX_7, PX_9, etc., up to PX_{21} (PCl_3Br_{18}).

The textbooks [1,2,3] and the handbook literature [8] contain brief references to the higher halides of phosphorus, but give extremely inadequate descriptions of them, as is also the case in the original papers dealing with these compounds. The data contained in the literature on these compounds is confined almost entirely to information on the methods of their preparation, their composition (based on chemical analysis), their external properties, their melting points, and a few chemical reactions [4,5,6,7,8,9]. Practically no light is shed upon the chemical nature of these compounds. All we find is the statement that these higher

halides of phosphorus, including the mixed halides, are polyhalides [1,17].

There is little if any experimental proof of this assertion. This is partly due to the fact that little research, expecially physicochemical research, has been done as yet upon these compounds, which makes it impossible to obtain an idea of the mechanism involved in the formation of these substances, their chemical nature, their structure, etc.

All the compounds made up of phosphorus, chlorine, and bromine (with the exception of $PCl_5 \cdot 5Br_2$)* have been prepared by reacting bromine with phosphorus trichloride. Compounds containing various percentages of bromine were produced, depending upon the ratios of the reagents employed. According to the literature, for example, nine compounds: PCl_4Br, PCl_3Br_2, PCl_2Br_3, $PClBr_4$, PCl_3Br_5, PCl_2Br_5, PCl_2Br_7, $PClBr_8$, and PCl_3Br_{18}, are formed when PCl_3 is reacted with bromine.

These data in the literature, obtained by various authors, often give rise to doubt as to their reliability, thus necessitating a more careful study of the $PCl_3 - Br_2$ system. Moreover, the mechanism involved in the formation of these compounds, which consist of the nonpolar, nonconducting bromine and the slightly polar, equally nonconducting phosphorus trichloride, is of considerable interest as a study of the nature of the bonds in systems constituted by nonpolar or slightly polar halogens and halides.

No physicochemical analysis has yet been made of the $PCl_3 - Br_2$ system. We have made a study of this system by the method of thermal analysis and have measured its specific conductance.

The fusibility curve we plotted for the $PCl_3 - Br_2$ system showed that two compounds are formed in this system: PCl_3Br_4 and PCl_3Br_{18}. We isolated both of these compounds and made a study of some of their properties.

EXPERIMENTAL

PCl_3 – a "chemically pure" preparation – was distilled two times. The preparation was kept in sealed ampoules. The boiling point of PCl_3 was 76.5°. The bromine – a commercial product – was purified as described in preceding reports [14].

Thermal analysis. The thermal analysis was performed in the vessel described in previous reports [15]. A thermometer graduated in tenths of a degree was secured to an asbestos stopper and immersed directly in the reaction mass, which made it possible to spot the thermal effects more precisely.

The $PCl_3 - Br_2$ system has a pronounced tendency toward supercooling. We have encountered cases in which the liquid did not solidify even when chilled to -30°, whereas the freezing point of the mixture should have been close to +20°. In such cases we added minute crystals of PCl_3Br_4 or PCl_3Br_{18}. We did not use the results of these tests in plotting the fusibility curve.

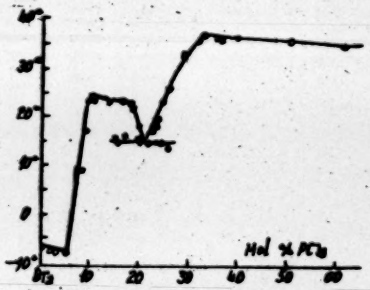

Fig. 1. Thermal analysis of the $PCl_3 - Br_2$ system.

The results of the thermal analysis of the $PCl_3 - Br_2$ system are shown in Table 2 and Fig. 1.

*Plotnikov and Yakubson prepared this compound by reacting PCl_5 the bromine [12].

TABLE 2

Thermal Analysis of the PCl_3 – Br_2 System

Molar % PCl_3	Arrest points		Molar % PCl_3	Arrest points	
	First	Second		First	Second
Bromine	-7.0	-7.8	20.21	16.2	15.2
2.15		-7.8	20.72	15.5	
3.57		-8.2	21.84		15.2
5.48		-8.4	22.78	17.5	
8.41	9.0		23.04	18.7	
9.13	17.0		23.61	20.0	
9.54	23.4		24.38	23.5	15.1
10.04	24.5		25.60	26.2	14.2
10.84	23.6		28.62	34.5	
13.48	23.0		31.70	36.5	
15.18		16.0 *	32.87	37.7	
15.71		15.0	34.81	37.3	
16.82	23.5		35.93	36.9	
17.27	–	16.5	38.90	37.3	
17.91	23.2		49.24	36.9	Liquid layer
18.58	22.2		61.78	36.6	
19.40		15.6	69.13	36.5	
19.72	18.5		76.48	36.8	
19.87		15.1	100.00	-112.5 *	

Adding up to 18 mol. % of PCl_3 to bromine is accompanied by an appreciable thermal effect. The arrest points are very sharp, with negligible supercooling up to 10 mol. % PCl_3 in the system. The first eutectic point is close to the crystallization temperature of pure bromine, namely, -8.4°.

Moreover, the crystallization temperature of the alloy rises as PCl_3 is added. The crystals formed are cherry-red needles that are as much as 2-3 cm long. A dystectic is observed at 10.04 mol% PCl_3 and 24.5°, the composition of which is that of the compound PCl_3Br_{18}. When the amount of PCl_3 added exceeds 10-12 mol. %, crystals settle out at a temperature close to 25°, their shape reminding one of PCl_3Br_{18} crystals, the rest of the liquid crystallizing at 15-16° in the shape of minute needles.

We encountered the greatest difficulties in determining the temperature of crystallization at concentrations ranging from ca. 11 to 20-22 mol.% PCl_3. We were frequently unable to secure the first and second arrest points for solutions of the same concentration; the first arrest points – at 11 to 19 mol. % PCl_3 – turned out to be very close together.

The second eutectic we discovered contained 20.7 mol.% PCl_3 and fused at 15.5°. Other second eutectic arrest points (at 15-16°) are observed on the fusibility curve, starting at a concentration of 15 mol.% PCl_3; this bears out our earlier conclusion that the maximum on the fusibility curve at 24.5° (for 10 mol. % PCl_3) constitutes a dystectic with the composition of PCl_3Br_{18}. After 20.7 mol.% PCl_3, the fusibility curve rises, reaching a maximum at 37.7° and 32.87 mol. % PCl_3, which corresponds to a compound with a composition of PCl_3Br_4.

When more than 33 mol.% of PCl_3 is added, all the way up to 90 mol.%, two immiscible liquid layers are observed to form. The upper layer consists of a saturated solution of PCl_3Br_4 in PCl_3. As is to be expected, the crystallization temperature of this layer is lower than the crystallization temperature of pure

* As given in the literature.

PCl_3, i.e., below -112.5°.

We made the following experiments to prove that this liquid, i.e., the upper layer, is actually a product of the dissolution of PCl_3Br_4 in PCl_3.

Experiment 1. A total of 4.08 mol.% of bromine was added to PCl_3. The bromine dissolved, giving rise to a brownish-red solution that did not stratify upon standing. When more bromine was added, up to 9.5 mol%, two layers were formed, crystals of PCl_3Br_4 settled out after 1 to 2 hours of standing; they were identified by chemical analysis (see page 484).

Experiment 2. Various, increasing amounts of PCl_3Br_4* were added to PCl_3, so as to constitute the following percentages, respectively: a) 1.02 mol.%; b) 2.55 mol.% (or 5.06 mol.% of Br_2, in terms of bromine); c) 4.76 mol.%, (or 9.15 mol.% Br_2).

A homogeneous solution was secured in the first two instances. In the third instance, the weight amount of PCl_3Br_4 did not dissolve completely even after standing (and agitation) for two hours and after heating. When a small amount of PCl_3 was then added so as to reduce the bromine concentration to 5.71 mol.%, and the solution was heated, all the crystals dissolved, a few crystals of PCl_3Br_4 settling out when the solution cooled, a saturated solution being formed as a brownish-red liquid.

We may therefore conclude that PCl_3Br_4 is sparingly soluble in PCl_3 and that a saturated solution is formed at a concentration of approximately 3 mol.% (which corresponds to about 5.5 mol.% of bromine).

When the mixture was cooled, minute crystals first settled out of the upper layer; as if they had infected a supercooled solution, they caused the entire lower layer, which consisted of PCl_3Br_4 as chemical analysis indicated (p.484), to crystallize. The bigger the upper layer, the easier was the crystallization of the lower layer, (almost without any supercooling at all).

We may conclude from the results of this thermal analysis that two compounds, PCl_3Br_{18} and PCl_3Br_4, are formed in the $PCl_3 - Br_2$ system.

Conductance of the $PCl_3 - Br_2$ system. The specific conductance of the $PCl_3 - Br_2$ system was measured in the usual manner. The mixture of PCl_3 and bromine was prepared by adding PCl_3 to bromine. The results of measurement are

TABLE 3

Specific Conductance of the $PCl_3 - Br_2$ System

Mol. % PCl_3	$\kappa_{25°} \cdot 10^2$	$\kappa_{30°} \cdot 10^2$	Mol.% PCl_3	$\kappa_{25°} \cdot 10^2$	$\kappa_{30°} \cdot 10^2$
Br_2	Nonconductor		19.00	6.35	
1.43	Nonconductor		20.03	6.25	7.00
3.79	2.68		22.17	5.72	
4.40	3.41		29.90	5.12	
6.38	4.18		31.52	5.12	
8.66	4.78	5.22	33.60	5.18	6.42
9.84	7.81		41.92	5.43	
9.90	7.90		50.12	5.53	
10.34	8.01	8.51	54.40	5.60	
11.35	7.98		56.58	5.61	6.62
12.90	7.61		65.57	5.61	6.62
14.28	7.41		68.62	5.61	6.62
16.68	6.85		100.0	Nonconductor	

* The preparation of PCl_3Br_4 is described on page 483.

given in Table 3 and Fig. 2. Bromine is a nonconductor, but when PCl_3 is added, the conductance rises sharply, attaining a maximum value of $8.01 \cdot 10^{-2}$ ohms^{-1}cm^{-1} at 10.34 mol.% PCl_3 (and at 25°), i.e., the conductance is a maximum for the coordination compound PCl_3Br_{18}. The specific conductance then drops off to a value of $5.12 \cdot 10^{-2}$ ohms^{-1} cm^{-1} at 30-32 mol.% PCl_3 (which is very close to the composition of the coordination compound PCl_3Br_4). When more than 33 mol.% of PCl_3 is added, two layers are formed, as indicated earlier, and the observed conductance applies only to the lower layer. Its conductance is $5.2\text{-}5.6 \cdot 10^{-2}$ ohms^{-1} cm^{-1}.

The upper layer, which is lighter in color and is a saturated solution of PCl_3Br_4 in PCl_3, is a nonconductor.

The lower layer – PCl_3Br_4 – is a good conductor in the molten as well as in the supercooled state.

The temperature coefficient of conductance is positive in the PCl_3 – bromine system.

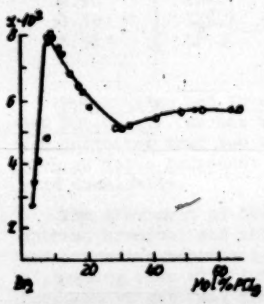

Fig. 2. Specific conductance of the PCl_3 – Br_2 system.

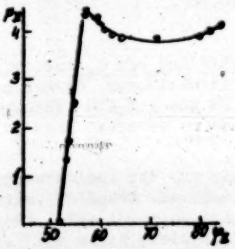

Fig. 3. Molar conductance of the PCl_3 – Br_2 system.

TABLE 4

Specific Gravity of the PCl_3 – Bromine System at 25°

Mol.% PCl_3	Specific gravity
Br	3.121
2.91	3.131
4.52	3.132
9.84	3.136
10.38	3.140
14.28	3.131
16.23	3.126
19.47	3.122
20.96	3.023
21.53	2.966

We determined the specific gravity at 25° of the PCl_3 –bromine system, and computed its molar conductance. As the PCl_3 concentration is increased, the specific gravity of this system begins to rise somewhat. The maximum specific gravity was observed at a PCl_3 concentration of 10.4 mol. %. Further addition of PCl_3 causes the specific gravity to drop. These facts indicate that the formation of the coordination compound PCl_3Br_{18} is accompanied by a shrinkage of the system.

The molar conductance of the PCl_3 – Br_2 system was computed in two ways: taking PCl_3 (φ_I, μ_I) as the electrolyte in the first, and taking bromine (φ_{II}, μ_{II}) as the electrolyte in the second. These figures are reproduced in Table 5 and Fig. 3.

As the system is diluted, the molar conductance, computed for PCl_3 as the electrolyte, begins to increase, but begins to drop off at $\varphi_I > 500$, slowly at first, and then very rapidly at high dilutions. The isotherm of molar conductance varies "anomalously" with concentration.

The inverse isotherm of molar conductance (φ_{II} and μ_{II}) is also anomalous; the molar conductance first rises and then drops as the solution is diluted.

Comparison of these two isotherms likewise indicates that a coordination compound is formed in the PCl_3 – bromine system.

TABLE 5

Molar Conductance of the PCl_3 – Br_2 System at 25°

Mol. % PCl_3	φ_I (in ml)	μ_I	Mol. % Br_2	φ_{II} (in ml)	μ_{II}
2.19	2332	0.573	97.81	52.2	0.123
3.79	1334	35.75	96.21	52.9	1.417
4.38	1150	36.23	95.62	53.1	1.81
6.66	776.6	37.36	93.34	54.1	2.60
9.91	501.4	39.60	90.09	55.8	4.41
11.35	445.7	35.20	88.65	56.6	4.51
14.28	350.2	25.95	85.72	58.4	4.33
16.57	301.4	20.65	83.43	59.9	4.10
19.01	262.4	16.66	80.99	61.6	3.91
20.09	250.3	15.64	79.91	63.7	3.98
26.14	213.9	11.98	73.86	70.9	3.97
29.90	184.7	9.44	70.10	79.0	4.04
31.52	175.7	8.99	68.48*	80.9	4.14
33.56*	165.6	8.52	66.44	83.4*	4.29

Preparation and investigation of the individual coordination compounds PCl_3Br_4 and PCl_3Br_{18}. As has been stated, the fusibility curve of the PCl_3 – Br_2 system indicates that two compounds, PCl_3Br_4 and PCl_3Br_{18}, exist in this system. Both of these compounds have been isolated in their individual states and analyzed chemically.

The treatment of the preparatinns for the quantitative determination of phosphorus, bromine, and chlorine, followed the lines of the procedure described in the preceding reports [11,15]. The chlorine and bromine were determined by precipitating them with $AgNO_3$. The mixed precipitate of AgCl and AgBr was dried to constant weight, and the AgBr was converted into AgCl by passing a current of chlorine over it; after which it was reweighed, and the per cent chlorine and bromine were computed.

Preparation of PCl_3Br_4. This compound was prepared from a mixture of PCl_3 and bromine that contained 57.42 mol.% of PCl_3. The upper layer was decanted, and the lower layer was allowed to solidify, after which it was recrystallized from a CCl_4 solution. The crystals were dried in a current of CO_2. The resulting crystals were orange-red with a bluish tinge. Their melting point was 37.7°, which is in good agreement with the data of thermal analysis (for the second dystectic).

Analysis results. 1.2714 g substance: 2.0673 g AgBr (0.8800 g Br). Found %: Br 69.22. PCl_3Br_4. Computed %: Br 69.94. 1.2714 g substance: 1.5548 g AgCl (0.3846 g Cl). Found %: Cl 23.96. PCl_3Br_4. Computed %: Cl 23.27. 1.2714 g substance: 61.3 ml 1 N KOH. Found %: P 6.51. PCl_3Br_4. Computed %: P 6.78.

In order to prove that the composition of the bottom layer, which consisted of the coordination compound PCl_3Br_4 according to the thermal analysis, was constant, we repeated the experiments involved in the preparation of this coordination compound, using PCl_3 – bromine mixtures that contained various percentages of PCl_3, viz.: a) 43.2 mol.%; b) 56.7 mol.%; and c) 68.6 mol.%.

In all these tests we secured PCl_3Br_4 as a product whose melting point and chemical analysis were identical with those given above.

Conductance of PCl_3Br_4. We used a product with a m.p. of 37.7° for these

*These values refer to the conductance of the lower layer, the composition of which is constant.

tests. We first endeavored to learn whether this coordination compound is a conductor in the solid state. We did this by placing the PCl_3Br_4 in the container used to measure conductance, melting it, and then chilling the container, trying to get the PCl_3Br_4 to solidify as a compact, more or less dense, mass, and then measuring its conductance at 25 and 30°. No conductance was discovered.

We then measured the conductance of this coordination compound in the liquid state at 35°*, 40°, 45°, and 50°. The minimum sound reading was very good ("sharp") at all these concentrations. The results are listed in Table 6.

TABLE 6

Specific Conductance of PCl_3Br_4

Temperature	35°	40°	45°	50°
Specific conductance, $ohms^{-1}\ cm^{-1}$	$1.82 \cdot 10^{-4}$	$7.09 \cdot 10^{-2}$	$7.42 \cdot 10^{-2}$	$6.59 \cdot 10^{-2}$

As we see from the figures in Table 6, PCl_3Br_4 is a good conductor of electricity. The conductance rises sharply between 35 and 40°, then rising slightly as the temperature is raised to 45°. Raising the temperature still higher, to 50°, causes the conductance to drop, apparently owing to the onset of thermal dissociation of the coordination compound, so that the conductance was not measured at any higher temperatures.

Preparation of PCl_3Br_{18}. This product was prepared in a small flask, fitted with a dropping funnel that passed through an asbestos stopper. The flask contained a weighed amount of PCl_3. A quantity of bromine sufficient to produce PCl_3Br_{18} was weighed into the funnel. The flask was chilled with ice or snow, and then the bromine was added to it drop by drop, with constant stirring. After all the bromine had been added, the flask was heated over a water bath at 28-30° with agitation, after which it was cooled; this caused elongated (up to 2 and 3 cm long) acicular crystals to settle out.

If not enough bromine is used, a mixture of crystals with the mother liquor will be secured. The latter is then removed by quickly transferring the mixture to a test tube with two inlets; the upper inlet was sealed, and the melt allowed to crystallize, after which the test tube was inverted and set aside to stand for several days to allow all the mother liquor to vitrify, and the test tube was resealed at the other inlet.

We used crystals with a m.p. of 24.5°, which agreed with the results of our thermal analysis for the first dystectic, for analysis and further investigation.

Analysis results: 0.8603 g substance: 1.8324 g AgBr (0.7797 g bromine). Found %: Br 90.62. PCl_3Br_{18}, computed %: Br 91.28; 0.8603 g substance: 0.2409 g AgCl (0.05957 g chlorine). Found %: Cl 6.92. PCl_3Br_{18}, computed %: Cl 6.78; 0.8603 g substance: 116.0 cm^3 0.1 N KOH. Found %: P 1.82. PCl_3Br_{18}, computed %: P 1.97.

Conductance of PCl_3Br_{18}. We used the preparation whose chemical analysis is cited above (m.p. 24.5°) in our conductance measurements.

The conductance of PCl_3Br_{18} was first measured at 13 and 20° (in the solid state), and then at 25-70° (the molten product).

We used the same procedure for the 13° and 20° measurements as in our measurements of the conductance of PCl_3Br_4.

As the figures in Table 7 indicate, PCl_3Br_{18} is a good conductor in the solid state.** The conductance of the molten product increases with the temperature,

* In this run we measured the conductance of a mixture of the solid state with a small amount of the molten substance.

** The measured values of conductance are only approximate since we could not be sure that the solid product was in perfect contact with the electrodes.

TABLE 7

Specific Conductance of PCl_3Br_{18}

Temperature	Specific conductance, ohms^{-1} cm^{-1}	Temperature	Specific conductance, ohms^{-1} cm^{-1}
13°	$6.27 \cdot 10^{-4}$	45°	$1.04 \cdot 10^{-1}$
20°	$1.53 \cdot 10^{-3}$	50°	$1.11 \cdot 10^{-1}$
25°	$8.01 \cdot 10^{-2}$	55°	$1.17 \cdot 10^{-1}$
30°	$8.51 \cdot 10^{-2}$	60°	$1.26 \cdot 10^{-1}$
35°	$9.15 \cdot 10^{-2}$	65°	$1.33 \cdot 10^{-1}$
40°	$9.86 \cdot 10^{-2}$	70°	$1.22 \cdot 10^{-1}$

TABLE 8

Specific Conductance of Eutectic Mixture Containing 19.96 mol.% PCl_3

Temperature	Specific conductance, ohms^{-1} cm^{-1}
20°	$5.43 \cdot 10^{-2}$
25	$6.25 \cdot 10^{-2}$
30	$7.00 \cdot 10^{-2}$
35	$8.00 \cdot 10^{-2}$
40	$8.42 \cdot 10^{-2}$
45	$9.35 \cdot 10^{-2}$
50	$9.68 \cdot 10^{-2}$
55	$1.01 \cdot 10^{-1}$

attaining the value of 0.13 ohm^{-1} cm^{-1} at 65°. When the temperature is raised still higher, to 70°, the conductance of PCl_3Br_{18} begins to drop, which must be due to the onset of thermal dissociation of this coordination compound.

The quite high conductance of PCl_3Br_{18}, which makes it a strong electrolyte, is worthy of note.

Specific conductance of the eutectic mixture. The $PCl_3 - Br_2$ system contains the compound PCl_3Br_8, according to the literature [6,7,1,2].

We did not find this compound, though the fusibility clearly shows that a eutectic is formed at 20.7 mol.% PCl_3, with a m.p. of 15.1-15.5°. We were therefore interested in measuring the conductance of such a eutectic mixture. We did this by preparing a mixture of PCl_3 and bromine containing 19.96 mol.% PCl_3,* and measuring its conductance at 20-55° (Table 8).

The conductances of PCl_3Br_4, PCl_3Br_{18}, and the eutectic mixture are listed together in Table 9 for the sake of comparison.

As Table 9 indicates, the conductance of the eutectic mixture lies in between the conductances of PCl_3Br_4 and PCl_3Br_{18} at the respective temperatures.

TABLE 9

Tested substance	Specific conductance at a temperature of:			
	40°	45°	50°	55°
PCl_3Br_{18}	$9.86 \cdot 10^{-2}$	$1.04 \cdot 10^{-1}$	$1.11 \cdot 10^{-1}$	$1.17 \cdot 10^{-1}$
PCl_3Br_4	$7.09 \cdot 10^{-2}$	$7.42 \cdot 10^{-2}$	$5.59 \cdot 10^{-2}$	
Eutectic mixture	$8.42 \cdot 10^{-2}$	$9.35 \cdot 10^{-2}$	$9.86 \cdot 10^{-2}$	$1.01 \cdot 10^{-1}$

Evaluation of results. As has been noted above, the literature contains descriptions of many compounds that are higher halides, and even mixed halides of phosphorus, especially those whose formulas can be represented by the general formula PCl_3Br_n, i.e., compounds that may be regarded as addition products of bromine and PCl_3.

In the most generalized form the composition of phosphorus chlorobromides is represented by the formula PCl_nBr_m. Several such chlorobromides of phosphorus, which are formed, according to various authors, when PCl_3 reacts with bromine, are listed in Table 1.

The data in the literature on the higher halides of phosphorus, especially the chlorobromides, are mostly rather indefinite and frequently contradictory.

*Which is quite close to the proportions of PCl_3 and bromine expressed by the formula PCl_3Br_8 (20 mol % PCl_3).

Most of them have been described almost exclusively as the result of researches of a preparative nature. A series of data in the literature on the compound with the composition of PCl_3Br_8 may be cited as examples of these contradictions.

Prinvault describes this substance as a reddish-brown oily liquid, which solidifies at 4-5°, forming brown needles with a metallic luster; it distils at 90° without decomposition, its vapor being colorless [6]. Michaelis, on the other hand, who synthesized this substance as Prinvault did – by mixing PCl_3 with bromine, writes that it consists of brown needles with a greenish tinge, which melt at about 25° and distill at 90° without decomposition, [7].

According to our data, the fusibility curve exhibited no compound with the composition of PCl_3Br_8 (20 mol.% PCl_3). A eutectic with 20.7 mol.% PCl_3 and a melting point of about 15.5° was found to exist in a concentration region extremely close to this composition.

These discrepancies referred to above and the gaps in the data cited in the literature for the higher halides of phosphorus may be attributed to the complexity of the transformations that PCl_3, PBr_3, PCl_5 and PBr_5 may enter into with one another or with the halogens. We must also bear in mind the appreciable reactivity of the phosphorus halides in these reactions, which is quite unexpected a priori, but has been fully confirmed by our previous investigations [11,15].

A variety of possible transformations in the PCl_3 – PBr_5, PCl_5 – PBr_3, and PCl_5-PBr_5 systems is cited in the papers by Milobedzki and his associates, as well as in papers by Renc, which we know only through the brief abstract published in Chemischer Zentralblatt [13,16].

An illustration of the complexity of the reactions that occur in these systems is the following equation cited in the abstract of Milobedzki's articles [13].

$$7PCl_5 + 3PBr_5 = 5PCl_{2.5}Br_{0.5} + 2PCl_{4.25}Br_{0.75} + 3PCl_{4.67}Br_{3.67}.$$

According to Milobedzki, the following compounds may be formed in the systems listed above: mixed trihalides – PCl_nBr_{3-n}; mixed pentahalides PCl_nBr_{5-n}; and the polyhalides PCl_2Br_n ($n > 3$) and PCl_3Br_n ($n = 4$-18). He includes PCl_3Br_{18} among compounds of the latter type. The abstract states [13] that Milobedzki prepared these "red polyhalides" (PCl_3Br_n) by reacting PCl_3 with bromine as well as reacting PCl_5 with PBr_5 (using 1 PCl_5 to 0.5-4 PBr_3 or 1 PBr_5 to 2-15 PCl_3).

The abstract does not state, unfortunately, exactly what compounds of this type Milobedzki prepared and what their properties were. All we can say is that PCl_3Br_{18} was first mentioned in this author's paper. The problem of the chemical nature of these compounds and of the mechanism of the reactions by which they are formed from PCl_3 and bromine is of considerable interest.

Compounds of the PCl_3Br_n type can hardly be classed as $PCl_3(Br_2)_n$ polyhalides, as this would contradict certain data cited in Milobedzki's paper. He discovered, for instance, that when PCl_3Br_4 – PCl_3Br_{18} compounds are evaporated in vacuum, they leave behind yellow crystals with the boundary formula of PCl_4Br. Milobedzki believes that when bromine reacts with PCl_3, first PCl_2Br and PCl_4Br are formed, which then add more bromine. Renc is of the same opinion. Moreover, when we consider the problem of the chemical nature of PCl_3Br_{18} and PCl_3Br_4, we must bear in mind the high conductivity of these compounds we have discovered. PCl_3Br_{18} is a conductor in the crystalline state. The conductance of molten PCl_3Br_{18} is of the same order of magnitude (0.13 ohm^{-1} cm^{-1}) as that of strong electrolytes (salts) in aqueous solutions.

Molten PCl_3Br_{18} is as good a conductor as PCl_3Br_4, though slightly less so (κ = 0.06-0.07 ohm^{-1} cm^{-1}). It should be remembered that the PCl_3 – bromine system exhibits high conductance even at low PCl_3 concentrations, of the order

of 3 mol.%, which is probably due to the formation of substances possessing the properties of strong electrolytes within this system. It must also be borne in mind that both of the initial substances from which these phosphorus chlorobromides are prepared – PCl_3 and bromine – are nonconductors by themselves; bromine molecules are nonpolar, while the dipole moment of PCl_3 is only 1.1 D.

All these facts are in agreement with the supposition we put forward above that the reaction of PCl_3 with bromine is a more complicated process than the direct addition of 4 to 18 molecules of bromine to the PCl_3 molecule. It may be that the initial process occurring in the PCl_3 – bromine system is an oxidation-reduction reaction, the products of which then add more or less bromine molecules to form coordination compounds.

Similar processes take place in the PCl_3 – iodine system. The electrolyte in this system is PCl_3I or $[PCl_4][ICl_2]$, which is the addition product of PCl_5 and iodine chloride, produced in the reaction: $PCl_5 + I_2 \rightleftarrows PCl_3 + 2ICl$ [15].

A study of the chemical nature of the phosphorus chlorobromides we have secured from the PCl_3 – bromine system and of the mechanism of their formation will be the subject of our future research.

We have found only two compounds, PCl_3Br_{18} and PCl_3Br_4, on the fusibility curve of the PCl_3 – bromine system. It cannot be asserted, however, that no chlorobromides with some other proportion of bromine (> 4 and < 18) can be formed in this system, though they are not shown on the fusibility curve for some reason or other. Phenomena of this sort have been repeatedly described in the literature – in papers by the N.S.Kurnakov school.

Our researches must also be continued along the lines of an endeavor to produce phosphorus chlorobromides with a composition that differs from those described in the present paper. The results of these investigations on the higher chlorobromides of phosphorus and, in general, on other higher phosphorus halides, a study of the chemical nature of this peculiar group of chemical compounds of phosphorus, which is almost wholly unexplored as yet, and an explanation of the properties of these higher halides of phosphorus as strong electrolytes, which approaches those of the salts, may likewise be of considerable interest, not only for the chemistry of phosphorus, but for the very much wider field of the chemistry of coordination compounds, as well as for the theory of electrolytes.

SUMMARY

1. A study has been made of the fusibility curve of the PCl_3 – bromine system. The fusibility curve exhibits two dystectics, the composition of which corresponds to that of the compounds PCl_3Br_{18} (m.p. 24.5°) and PCl_3Br_4 (m.p. 37.5°). At percentages of PCl_3 in excess of 33 mol.%, up to 90 mol.% PCl_3, two immiscible layers are formed in the liquid.

2. The coordination compounds PCl_3Br_{18} and PCl_3Br_4 have been secured in their individual states, and their conductance has been measured. The specific conductance of PCl_3Br_4 is $7.42 \cdot 10^{-2}$ ohm^{-1} cm^{-1} at 45°. It drops off at higher temperatures. The specific conductance of PCl_3Br_{18} rises with temperature, attaining its maximum value of $1.33 \cdot 10^{-1}$ ohm^{-1} cm^{-1} at 65°, after which it decreases.

3. The chemical nature and the mechanism of the formation of PCl_3Br_{18} and PCl_3Br_4 are discussed.

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*See CB translation p. 997 ff.
**See CB translation p. 797 ff.

THERMODYNAMIC FUNCTIONS

Al_4C_3, Si, SiO_2, SiC, AlF_3 AND Na_3AlF_6

L. I. Ivanova

1. INTRODUCTION

The thermodynamic functions of aluminum carbide (Al_4C_3), crystalline silicon (Si), silica (SiO_2), silicon carbide (SiC), aluminum fluoride (AlF_3), and cryolite (Na_3AlF_6) have been calculated for the temperatures 50, 100, 200.... 1300° K. The heat contents ($H_T - H_0$) have been computed from Kirchhoff's equation:

$$H_T = H_0 + \int_0^T \sum nC_p dT. \qquad (1)$$

All the heat capacities cited in the literature for these compounds or elements have been collated and critically evaluated for the calculation of

$$\int_0^T \sum nC_p dT.$$

The heat-capacity curve was plotted from these values of heat capacity.

$$\int_0^T \sum n\, C_p\, d\, T$$

was computed graphically by integrating the area bounded by the heat-capacity curve and the axes of abscissas and ordinates for the given value of T. The entropy was calculated from the equation:

$$S_T = S_0 + \int_0^T \frac{\sum n\, C_p\, d\, T}{T}. \qquad (2)$$

If we know the values of $H_T - H_0$ and $S_T - S_0$, we can find the value of the free energy $F_T - F_0$ from the formula:

$$F_T - F_0 = \int_0^T \sum n\, C_p\, dT - T \int_0^T \frac{\sum n\, C_p}{T}\, dT \qquad (3)$$

or

$$F_T - F_0 = (H_T - H_0) - T\,(S_T - S_0) \qquad (4)$$

and, hence, find the maximum work, since the work function equals the loss of free energy:

$$A = -\,(F_T - F_0) \qquad (5)$$

Knowing the work function A, we can calculate the equilibrium constant from the formula:

$$\log K = \frac{A}{2.3\,RT}. \qquad (6)$$

The calculated values of the thermodynamic functions are given in the subjoined tables. In these tables, the heat capacities are expressed in calories, the heat content (enthalpy) in calories, the free energy in calories, and the entropy in calories per degree. Temperatures are given on the absolute Kelvin scale (° K). In our computations we have employed thermochemical notation, i.e., "+" signifies the evolution of heat, and "−" the absorption of heat.

2. Calculation of the Thermodynamic Functions

Aluminum carbide. The only available experimental data for the heat capacities of aluminum carbide are the observations of Satoh [1], made with an ice calorimeter. Satoh gives the following equation for the true heat capacity of aluminum carbide, applicable in the temperature range from 0 to 320°C:

$$c = 0.2282 + 2.12\cdot10^{-4}\,t - 2.842\cdot10^{-8}\,t^2, \qquad (7)$$

where t is the temperature in degrees Centigrade. When we convert the heat capacity of Al_4C_3 into the molar heat capacity and express the temperature in degrees Kelvin, we get;

T	1/7 C_p
300	4.77
400	5.23
500	5.60

For want of other experimental data on the heat capacity of Al_4C_3, we resolved to compute the latter from the Debye equation:

$$C_p = 3R\left[\frac{4}{5}n^4\left(\frac{T}{\beta\nu}\right)^3 - \frac{3\frac{\beta\nu}{T}}{e^{\frac{\beta\nu}{T}}-1} - 12\frac{\beta\nu}{T}\sum_{n=1}^{n=\infty} e^{-n\frac{\beta\nu}{T}}\left(\frac{1}{n\frac{\beta\nu}{T}} + \frac{3}{n^2\left(\frac{\beta\nu}{T}\right)^2} + \frac{6}{n^3\left(\frac{\beta\nu}{T}\right)^3} + \dots\right)\right] \qquad (8)$$

where ν is the atoms' own vibration frequency, T is the absolute temperature, β = h/k, h being the Planck constant, and k the Boltzman constant.

The following data were used to compute the heat capacities of aluminun carbide:

Atomic weight of aluminum: $A_1 = 26.97$;
Density of aluminum [2, p.128]: $d_1 = 2.7$;
Melting point of aluminum, absolute temperature [2, p.128]: $T_{S_1} = 660 + 273 = 933°$ K;
Atomic weight of carbon: $A_2 = 12$.
Density of carbon: [2, p.128] $d_2 = 2.25$.
Melting point of carbon, absolute temperature [2, p.128]: $T_{S_2} = 3500 + 273 = 3773°$ K;
Absolute temperature at which aluminum carbide sublimes [3]: $T_S = 2200 + 273 = 2473°$ K.

The $\beta\nu$ of the elements was computed from the Lindemann equation:

$$\beta v = 135 \sqrt{\frac{T S_1}{M v^{2/3}}}, \qquad (9)$$

where v is the atomic volume, M is the molecular weight, and T is the melting point in °K.

For compounds βv was recomputed from Koref's equation:

$$\beta v' = \beta v \sqrt{\frac{T S_1}{T S}} . \qquad (10)$$

In computing the atomic heat capacities C_v for the given values of $\frac{\beta v}{T}$ from the Debye equation, we made use of the available ready-reference tables [4, p. 705]. The molar heat capacity of the solid compound was calculated as the sum of the atomic heat capacities of the elements constituting this compound. After we had found the C_v for the compound, we obtained its C_p from Nernst's empirical equation:

$$C_p = C_v = 0.0214 \frac{T}{T_S} C_p^2 , \qquad (11)$$

where T_S is the melting point on the absolute scale. The heat capacities calculated in this manner are given in Table 1.

The curve for 1/7 $C_p Al_4C_3$, from the theoretically computed values, is reproduced in Fig. 1, together with the curve for 1/7 C_p plotted from Satoh's experimental values. The experimental values of heat capacity are close to the theoretical ones at 300, 400, and 500°K. The thermodynamic functions of Al_4C_3, calculated as described above from these theoretical values of the heat capacity, are listed in Table 1.*

TABLE 1

Thermodynamic Functions of Aluminum Carbide (1/7 Al_4C_3)

T °K	C_p	$H_T - H_0$	$S_T - S_0$	$-F_T - F_0$
50	0.16	(4)	(0.08)	(0)
100	1.00	33	0.41	8
200	3.07	235	1.69	103
300	4.48	614	3.19	343
400	5.46	1107	4.62	741
500	6.14	1691	5.92	1269
600	6.74	2335	7.09	1919
700	7.29	3037	8.17	2682
800	7.83	3792	9.18	3552
900	8.38	4607	10.14	4519
1000	8.94	5469	11.05	5581
1100	9.54	6394	11.93	6729
1200	10.17	7379	12.79	7969
1300	10.92	8434	13.64	9298

Silicon. In calculating the thermodynamic functions of silicon, we made use of the experimental values of the heat capacity obtained by Dewar [5, p.1247], Roussel [5 p.1247], Weber [5], Wiegland [5], Nernst and Schwers [5], Magnus, [4, p.888], Anderson [8, p. [1169], and others.

We likewise made use of Kelley's formula [7]:

$$C_p = 5.74 + 6.17 \cdot 10^{-4} T - \frac{101000}{T^2} , \qquad (12)$$

which holds good within 2% between 273° K and 1173° K.

The heat capacities obtained by the different authors were laid out on graph paper, and the heat capacity curve was plotted. There are two known modifications of silicon: crystalline and amorphous. The heat capacity of crystalline silicon differs but slightly from that of the amorphous modification. We computed the heat capacity of crystalline silicon theoretically, from the Debye equation described above [8], in order to compare it with the experimental values. We employed the following data:

* Recomputed on the basis of 1 gram atom.

Atomic weight of silicon: A = 28.06; Density of crystalline silicon [4, p. 285]: d = 2.49; melting point of silicon, absolute temperature [2, p. 129]: T_s = 1420 + 273 = 1693° K.

The curve of the experimental values of the heat capacity and the curve of the heat capacities as calculated from the theoretical Debye equation are reproduced in Fig. 2. As the figure shows, the heat capacities computed theoretically are in good agreement with the experimental values. Ruff and Konschak [8] consider that the Cp of silicon is constant in the liquid state, equaling 6.62.

We calculated the thermodynamic functions (heat content, entropy, and free energy) for the crystalline modification. Silicon melts at a temperature in the neighborhood of 1693° K [2, p.129]. Its heat of fusion has not been measured as yet, but it approximates 3714 cal [9, p.223]. The resulting values of the thermodynamic functions of crystalline silicon are listed in Table 2.

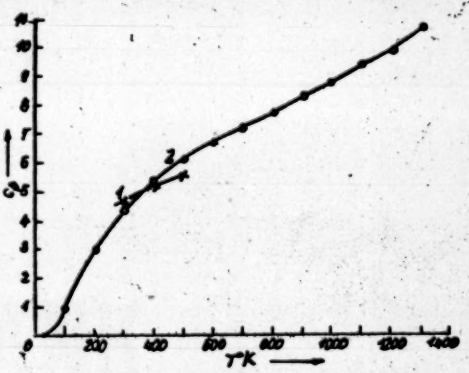

Fig. 1. Variation of the heat capacity of aluminum carbide with temperature ($1/7\ C_p\ Al_4C_3$)

1-Satoh's observations; 2-computed theoretically.

Silica. Table 3 gives the thermodynamic functions of silica. In computing these thermodynamic functions we made use of the experimental heat capacities observed by Nernst [5], Koref [5], Magnus [5], White [5], Bornemann and Hengstenberg [5], Whitley [10], Perry and Rocks [4], Kohn [6], and Roth and Bertram, [6]. We also made use of Kelley's formula [7]:

$$C_p = 10.87 + 8.712 \cdot 10^{-3} T - \frac{241200}{T^2}, \quad (13)$$

for α-quartz, which holds good within 1% throughout the range 273° K to 848° K, and of the Kelley formula:

$$C_p = 10.97 + 5.50 \cdot 10^{-3}\ T, \quad (14)$$

for β-quartz, which holds good within 3.5% throughout the range from 848° K to 1873° K.

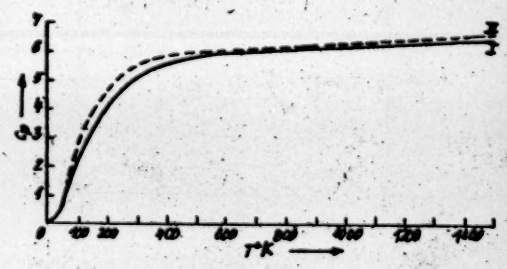

Fig. 2. Variation of the heat capacity of crystalline silicon with temperature.

I-experimental observations; II-computed theoretically.

β-Quartz is transformed into α-quartz at a temperature of 848° K (or 575° C). The heat of transition is negligible, totaling only 4 cal [11, p. 258].

Silicon carbide. The thermodynamic functions of silicon carbide, listed in Table 4, have been computed from the

TABLE 2

Thermodynamic Functions of Crystalline Silicon (Si)

T° K	Cp	$H_T - H_o$	$S_T - S_o$	$-(F_T - F_o)$
50	0.55	6.5	0.137	0.35
100	2.00	70	0.912	21.2
200	3.95	368	2.899	212
300	4.98	814	4.717	601
400	5.55	1340	6.240	1156
500	5.80	1908	7.514	1849
600	5.87	2490	8.583	2660
700	5.97	3083	9.498	3565
800	6.08	3686	10.305	4558
900	6.17	4298	11.027	5626
1000	6.26	4920	11.683	6763
1100	6.34	5550	12.284	7962
1200	6.41	6187	12.839	9220
1300	6.48	6832	13.355	10533
1400	6.55	7483	13.838	11890
1500	6.62	8141	14.288	13291
1600	6.69	8806	14.718	14730
1693	6.75	9431	15.099	16130
1693	6.62	13145	17.292	16130
1700	6.62	13191	17.319	16251
1800	6.62	13853	17.639	17905
1900	6.62	14515	17.999	19683
2000	6.62	15177	18.339	21501

experimental values of the heat capacity obtained by Nernst and Schwers [5], Guncher [5], Roussel [5], Weigel [5], Magnus [4], and others.

We also used Kelley's formula:

$$C_p = 8.89 + 2.91 \times 10^{-3} T - \frac{284000}{T^2} \qquad (15)$$

which holds good within 2% throughout the range from 273 to 1623 °K.

Aluminum fluoride. The only measurements of the heat capacity of aluminum fluoride recorded in the literature are those of V.S.Lyashenko [12], covering the region from 290 to 1305° K, and a single value of mean heat capacity, observed by Baud [13] in the interval from 288 to 306° K. V. S. Lyashenko gives the formula:

$$C_T = 24.9418 + 3.432 \cdot 10^{-2} T - 1.8746 \cdot 10^{-5} T^2 \qquad (16)$$

TABLE 3

Thermodynamic Functions of Quartz ($^1/_3$ SiO_2)

T° K	Cp	$H_T - H_o$	$S_T - S_o$	$-(F_T - F_o)$
50	0.52	6	0.13	0.5
100	1.24	50	0.70	20
200	2.70	247	1.99	151
300	3.68	565	3.28	419
400	4.31	964	4.43	808
500	4.75	1417	5.44	1303
600	5.02	1906	6.34	1898
700	5.30	2422	7.14	2576
800	5.75	2974	7.88	3330
848	5.90	3253	8.22	3718
848	5.20	3260	8.23	3718
900	5.38	3535	8.54	4151
1000	5.55	4081	9.11	5029
1100	5.71	4644	9.65	5971
1200	5.80	5220	10.15	6960
1300	6.00	5810	10.62	7996
1400	6.20	6421	11.07	9077
1500	6.40	7047	11.50	10203
1600	6.58	7691	11.91	11365
1700	6.80	8360	12.32	12584
1800	6.96	9047	12.71	13831
1900	7.13	9751	13.09	15120

TABLE 4

Thermodynamic Functions of Silicon Carbide ($^1/_2$ SiC)

T° K	Cp	$H_T - H_o$	$S_T - S_o$	$-(F_T - F_o)$
50	0.04	0.5	0.02	0.5
100	0.55	15.2	0.18	2.8
200	1.91	123	0.93	63
300	3.30	398	1.95	187
400	4.14	770	3.01	434
500	4.60	1207	3.98	783
600	4.92	1683	4.84	1221
700	5.17	2187	5.62	1747
800	5.39	2715	6.32	2341
900	5.58	3264	6.97	3009
1000	5.76	3831	7.57	3739
1100	5.91	4414	8.12	4518
1200	6.07	5013	8.64	5355
1300	6.22	5628	9.13	6241
1400	6.41	6266	9.50	7034
1500	6.56	6915	10.05	8160
1600	6.71	7578	10.48	9510
1700	6.87	8257	10.89	10256
1800	7.02	8953	11.33	11441
1900	7.17	9762	11.71	12487
2000	7.32	10486	12.07	13654

The heat capacities of aluminum fluoride computed from Lyashenko's formula are listed in Table 5 together with the heat capacities of other fluorides.

TABLE 5

T° K	½ C_pKF	½ C_p NaF	⅓ C_p BaF_2	⅓ C_p MgF_2	¼ C_p AlF_3
100	3.49	2.67	–	–	3.1
200	5.31	4.83	–	–	4.2
300	5.90	5.51	–	–	4.5
400	6.13	5.85	–	–	4.9
500	6.29	6.09	–	–	5.2
600	6.44	6.32	6.66	5.56	5.7
700	6.57	6.51	6.82	5.96	6.1
800	6.67	6.69	7.01	6.41	6.5
900	6.76	6.85	7.25	6.83	6.8
1000	6.82	6.98	7.52	7.26	7.4
1100	6.88	7.08	7.82	7.70	7.8
1200	8.20	7.15	8.12	8.16	8.2
1300	8.200	8.80	8.52	8.62	8.6

Table 5 indicates that the heat capacities of aluminum fluoride, in terms of the number of atoms in the AlF_3 molecule, are close to the corresponding values of heat capacity for other fluorides.

The thermodynamic functions of aluminum fluoride listed in Table 6 have been calculated from V.S.Lyashenko's values of the heat capacity.

The heat capacity of aluminum fluoride at low temperature has been calculated from the Debye equation.

Cryolite. The heat capacity of cryolite has been investigated by Roth and Bertram [18]. They found that cryolite has two modifications: the α-form up to 838° K, and the β-form from 838° K to the melting point. The data of A.N.Krestovnikov and G.A.Karetnikov [15] on the heat capacity of cryolite were published in 1934, and those of V.S.Lyashenko [12] in 1935.

V.S.Lyashenko's research confirmed the existence of two modifications of cryolite. He gives two equations for the true heat capacity of cryolite. One equation applies to the α-modification, applicable from 293 to 838° K, is:

TABLE 6

Thermodynamic Functions of Aluminum Fluoride (¼ AlF_3)

T° K	C_p	$H_T - H_o$	$S_T - S_o$	$-(F_T - F_o)$
50	1.0	12	0.25	0.5
100	3.1	114	1.52	38
200	4.2	479	4.10	341
300	4.5	914	5.92	862
400	4.9	1424	7.28	1488
500	5.2	1915	8.41	2290
600	5.7	2434	9.40	3206
700	6.1	3024	10.31	4193
800	6.5	3654	11.16	5274
900	6.8	4319	11.93	6418
1000	7.4	5029	12.67	7611
1100	7.8	5789	13.40	8951
1200	8.2	6599	14.18	10517
1300	8.6	7229	14.77	11972

$$C_T = 35.882 + 0.63339 \cdot T - 2.5131 \cdot 10^{-5} T^2, \qquad (17)$$

while the other, for the beta modification, applicable from 838° K to the melting point, is:

$$C_T = 68.9208 + 0.004002\ T. \qquad (18)$$

A.N.Krestovnikov and G.A.Karetnikov give a single equation for the true heat capacity of cryolite, applicable from 15 to 900° C:

$$C_t = 0.24595 + 2.51 \cdot 10^{-4}\, t - 1.255 \cdot 10^{-7}\, t^2, \qquad (19)$$

where t is the temperature in °C. They make no mention of any modifications of cryolite.

The curves of the heat capacity of cryolite, according to A.N.Krestovnikov and G.A.Karetnikov and according to V.S.Lyashenko, are reproduced in Fig. 3.

The values of the heat capacity of cryolite observed by Roth and Bertram are somewhat higher. Lyashenko attributes this to the fact that Roth and Bertram used a cryolite that did not have the stoichiometrical composition. In computing the thermodynamic functions of cryolite listed in Table 7, we relied upon the data of V.S.Lyashenko.

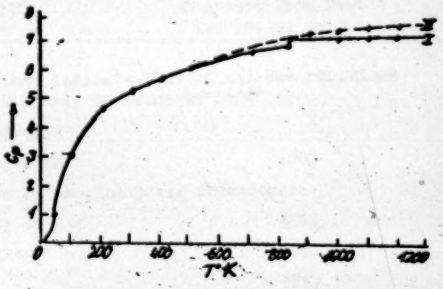

Fig. 3. Variation of the heat capacity of cryolite with temperature ($^1/_{10}$ C_p Na_3AlF_6)

I-Lyashenko's observations; II-Krestovnikov's and Keretnikov's observations.

3. Calculation of Maximum Work and Equilibrium Constants

The thermodynamic functions we computed were used to calculate the maximum work and equilibrium constants of reactions between silica and a cryolite-alumina melt at 1300° K with carbon and aluminum present.

These reactions are of considerable importance in the electrolytic production of aluminum-silicon alloys by electrolyzing cryolite-alumina melts to which silica has been added.

Table 8 gives the calculated values of the equilibrium constants for the conceivable reactions that may take place in the electrolytic bath at 1027° C (or 1300° K). The calculated values of the equilibrium constants enable one to judge the probability of any one reaction occurring at the given temperature.

TABLE 7

Thermodynamic Functions of Cryolite ($^1/_{10}$ Na_3AlF_6)

T° K	C_p	$H_T - H_o$	$S_T - S_o$	$-(F_T - F_o)$
50	1.00	12	0.25	0.5
100	3.00	112	1.50	38
200	4.75	497	4.16	335
300	5.23	992	6.21	871
400	5.71	1532	7.80	1588
500	6.13	2122	9.11	2433
600	6.49	2750	10.26	3406
700	6.82	3392	11.28	4504
800	7.05	4082	12.21	5686
838	7.13	4350	12.54	6158
838	7.23	4350	12.54	6158
900	7.25	4797	13.05	6948
1000	7.29	5524	13.81	8286
1100	7.33	6254	14.51	9707
1200	7.37	6989	15.14	11179
1300	7.41	7728	15.73	12721

The values of the thermodynamic functions computed by Terebesi [18] for alumina (Al_2O_3), aluminum (Al), oxygen (O_2), and carbon (C) and computed by Johnson and Davis [10] for carbon monoxide (CO) were used in calculating the equilibrium constants.

For SiF_4 we used the values calculated by I.G.Ryss [19] from spectographic observations. We likewise used the following values of the heats of formation:

Compound	Q_{273}, cal	Author
Al_2O_3	+398000	Roth [17]
SiO_2	+208300	Roth [17]
Al_4C_3	+40000	Roth [17]
SiC	+31000	Wartenberg [20]
NaF	+136000	Wartenberg [21]
SiF_4	+360300	Wartenberg [20]
AlF_3	+331500	Wartenberg [21]
Na_3AlF_6	+743851	Baud [22, p. 430]
Na_2O	+100260	Beketov [23]
CO	+26570	Computed from Hess's law [9, p. 171].

The values of the equilibrium constant indicate that of all the reactions enumerated above, the following are most likely to occur at 1300° K:

1. The reduction of silica by aluminum:

$$3SiO_2 + 4Al = 2Al_2O_3 + 3Si. \quad (20)$$

2. The formation of silicon carbide by the following reactions:

$$3SiO_2 + Al_4C_3 = 2Al_2O_3 + 3SiC, \quad (21)$$

$$3Si + Al_4C_3 = 4Al + 3SiC, \quad (22)$$

$$Si + C = SiC. \quad (23)$$

3. The formation of silicon tetrafluoride as the result of the reaction of silicon with aluminum fluoride:

$$3SiO_2 + 4AlF_3 = 2Al_2O_3 + 3SiF_4. \quad (24)$$

TABLE 8

No.	Reaction	Maximum work, cal	$K_p = 1300$
1	$3SiO_2 + 4AL = 2Al_2O_3 + 3Si$	+ 143183	$1.20 \cdot 10^{24}$
2	$3SiO_2 + Al_4C_3 = 2Al_2O_3 + 3SiC$	+ 186394	$2.20 \cdot 10^{31}$
3	$3Si + Al_4C_3 = 4Al + 3SiC$	+ 51701	$4.95 \cdot 10^{8}$
4	$Si + C = SiC$	+ 27891	$4.90 \cdot 10^{4}$
5	$3SiO_2 + 4AlF_3 = 2Al_2O_3 + 3SiF_4$	+ 42579	$1.45 \cdot 10^{7}$
6	$3SiO_2 + 4Na_3AlF_6 = 2Al_2O_3 + 12NaF + 3SiF_4$.	+ 19643	$2.00 \cdot 10^{3}$
7	$3SiC + 4Na_3AlF_6 = 12NaF + 3SiF_4 + Al_4C_3$..	− 172413	$1.02 \cdot 10^{-28}$
8	$3SiC + 4AlF_3 = 3SiF_4 + Al_4C_3$	− 141873	$1.38 \cdot 10^{-24}$
9	$3Si + 4AlF_3 = 4Al + 3SiF_4$	− 88133	$1.51 \cdot 10^{-15}$
10	$SiO_2 + 4NaF = 2Na_2O + SiF_4$	−	$1.78 \cdot 10^{-25}$
11	$SiO_2 + 2C = Si + 2CO$	− 47236	$1.13 \cdot 10^{-8}$

Recent experiments [24] have confirmed the correctness of the conclusions drawn from the thermodynamic calculations. It should be noted that these thermodynamic calculations make no allowance for the rates of reaction, which may play a decisive role in practice at times.

SUMMARY

1. The heat capacities of aluminum carbide (Al_4C_3) and crystalline silicon (Si) have been computed theoretically.

2. The thermodynamic functions of aluminum carbide (Al_4C_3), crystalline

silicon (Si), quartz (SiO_2), silicon carbide (SiC), aluminum fluoride (AlF_3), and cryolite (Na_3AlF_6) have been calculated.

3. These calculated thermodynamic functions have been used to compute the maximum work and the equilibrium constants of various reactions in the molten bath that contains cryolite, alumina, silica, metallic aluminum, and carbon, and to ascertain which are the most probable reactions at a temperature of 1300° K.

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THE THERMAL ANALYSIS OF THE BINARY SYSTEMS

$CdBr_2$ - $ZnBr_2$, $CdBr_2$ - $PbBr_2$, AND $CdBr_2$ - AgBr

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1. Comparatively little experimental material is available on the chemistry of melts, and hence, even less in the way of theoretical generalizations. The reason for this is the difficulty of experimentation, due principally to the high temperatures involved.

Behavior patterns that are not open to doubt in liquid solutions under ordinary conditions do not always hold good for systems in which the solvent is a molten salt.

The author has investigated a series of decomposition voltages of bromides: of zinc, cadmium, lead, copper, silver, cobalt, nickel, and bismuth dissolved in molten cadmium bromide [1]. The discrepancies between this series and the series of the same metals in water as well as in other solvents indicates the undoubted influence of the solvents on the metal potentials. We were therefore interested in a further study of the reaction between a solvent – particularly cadmium bromide – with the bromides dissolved in it. With this in mind we made a thermal analysis of the following systems: $CdBr_2$ – $ZnBr_2$, $CdBr_2$ – $PbBr_2$, $CdBr_2$ – AgBr.

2. Preparation of the salts.

a) $CdBr_2$. Chemically pure cadmium bromide was sublimed in a current of anhydrous CO_2 to desiccate it.

b) $ZnBr_2$. Chemically pure zinc was dissolved in chemically pure hydrobromic acid. The solution was evaporated. The salt was melted by slow heating, and then distilled from a refractory retort into a test tube, which was sealed when it was filled.

c) $PbBr_2$. Lead bromide was precipitated out of a solution of chemically pure lead acetate by chemically pure hydrobromic acid. The $PbBr_2$ was recrystallized from a hot aqueous solution and then dried to constant weight at 110-120°. It was kept in glass-stopped ampoules in a desiccator.

d) AgBr. Silver bromide was precipitated by chemically pure hydrobromic acid from a solution of chemically pure silver nitrate in complete darkness. The product was washed after decantation, still in darkness, until the bromine ions had been removed and then dried to constant weight at 110-120°. It was kept in glass-stoppered ampoules in a desiccator kept in the dark.

EXPERIMENTAL

The installation used for making thermal analyses consisted of an electric crucible furnace that was well insulated with asbestos against rapid cooling. The

salts were melted in a quartz test tube into which a high-degree thermometer projected. The molten salts were carefully stirred while cooling with a stirrer made of platinum wire. The thermometer was graduated in one-degree divisions. The readings were accurate to 1°. The mean cooling rate was 5° per minute throughout the 350-600° range. Readings were taken every half minute. The thermometer was calibrated according to the following pure substances:

Tin – melting point	231.8° C
Lead – melting point	327.3
Zinc – melting point	410.5
Antimony – melting point ...	630.5.

$CdBr_2$-$ZnBr_2$ System

In our investigations we found the melting point of $CdBr_2$ to be 575°. Nacken has found the melting point of pure cadmium bromide to be 587° [5]. Other authors give the following figures for the melting point of this bromide: Carnelley [6], 571°; Weber [7], 580°; Craetz [8], 585°. The discrepancies between the values testify to varying states of purity of the salt and to different degrees of accuracy of measurement by the various researchers.

TABLE 1

Per cent by weight		Temp. of beginning of crystallization	Temp. of eutectic crystallization
$CdBr_2$	$ZnBr_2$		
0.00	100.00	395	–
5.92	94.08	390	–
17.13	82.87	377	364
27.50	72.50	376	364
34.57	65.43	402	364
51.49	48.51	457	364
64.07	35.93	495	364
79.00	21.00	511	–
100	0.00	575	–

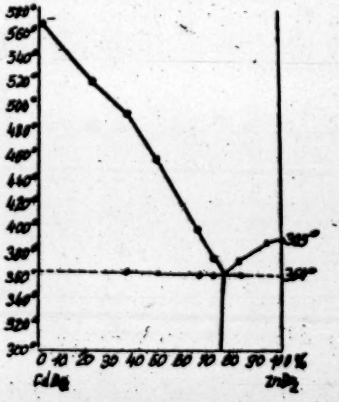

Fig. 1

In our investigations zinc bromide melted at 395°. The values in the literature are: Hampe [9], 394°; Craetz, 390°; Etard [10], 375°.

Molten $ZnBr_2$ exhibits considerable supercooling when it cools down: the contents of the test tube first solidified into a glasslike mass, after which the salt crystallized, with the evolution of a fairly large amount of heat. As $CdBr_2$ is added the supercooling diminishes, being eliminated altogether by vigorous stirring.

Our results are listed in Table 1, and the phase diagram is reproduced in Fig. 1.

The phase diagram exhibits a eutectic point at 364° and a composition of 75.5% $ZnBr_2$ and 24.5% $CdBr_2$. Zinc bromide is soluble in all proportions in molten cadmium bromide; there are no chemical compounds formed between $CdBr_2$ and $ZnBr_2$.

$CdBr_2$-$PbBr_2$ System

The melting point of the lead bromide we used in our investigation was found to be 375°. In the literature, this melting point is given as 363° by Ramsay [11]

and others. In contrast to the preceding system, the phenomenon of supercooling may be readily avoided during the cooling of molten lead bromide, or of a mixture of the latter with molten cadmium bromide, by stirring. The analysis data are given in Table 2, and the phase diagram in Fig. 2.

TABLE 2

Per cent by weight		Temp. of beginning of crystallization	Temp. of eutectic crystallization
$CdBr_2$	$PbBr_2$		
0.00	100.00	375	–
2.74	97.26	371	–
15.50	84.40	356	344
21.80	78.20	360	344
28.50	71.50	426	344
46.90	53.10	486	344
60.13	39.87	512	344
78.59	21.41	542	–
88.98	11.02	536	–

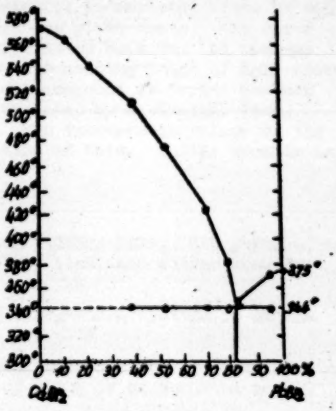

Fig. 2.

The phase diagram of this system, like that of the preceding one, is of the simplest type. The eutectic point is situated at 344° and a composition of 82% $PbBr_2$ and 18% $CdBr_2$. The solubility of each constituent in the other is unlimited. No chemical compounds are formed.

System $CdBr_2$–AgBr

We found the melting point of silver bromide to be 424°. Carnelley gives it as 427 ± 4.5°, while Ramsay and Eumorfopoulos give 424° [12].

TABLE 3

Per cent by weight		Temperature of beginning of crystallization
AgBr	$CdBr_2$	
100.00	0.00	424
93.82	6.18	429
85.50	14.50	445
79.15	20.85	449
68.00	32.00	449
58.90	41.10	449
56.47	43.53	449
50.00	50.00	456
43.42	56.58	468
40.38	59.62	479
33.63	66.37	498
26.28	73.72	515
13.05	86.95	546

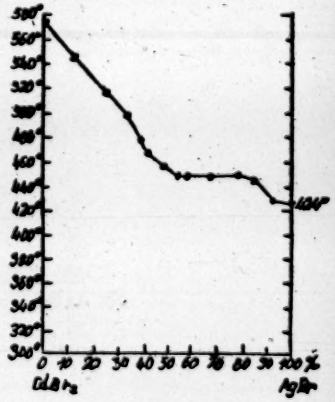

Fig. 3.

Unexpected difficulties were encountered in the investigation of this system: the volume of the molten mixture increased considerably upon solidification, always breaking the quartz test tube. We therefore had to confine our observations to the temperature at which crystallization set in, making no study of further cooling. The research data are listed in Table 3 and shown graphically in Fig. 3.

The fusibility diagram of the $CdBr_2$–AgBr system is incomplete, since we did not plot the cooling curves completely for the reasons given above. The curve has been plotted from the points at which crystallization sets in. As cadmium bromide is gradually added to the silver bromide, the melting point of AgBr rises, contrary to expectation. It may be that a chemical compound is formed between the constituents along the portion of the curve depicted by a straight line, practically all of which is dissociated at 449°. The increase in volume of the mixture upon solidification is indirect confirmation of this. Silver bromide is indefinitely soluble in molten cadmium bromide.

SUMMARY

Thermal analyses have been made of the systems: $CdBr_2$–$ZnBr_2$, $CdBr_2$–$PbBr_2$, and $CdBr_2$–AgBr, to ascertain the solubility of zinc, lead, and silver bromides in cadmium bromide as the solvent.

1. The phase diagram of the $CdBr_2$–$PbBr_2$ and $CdBr_2$–$ZnBr_2$ systems is of the simplest type, with a single eutectic.

2. The phase diagram of the $CdBr_2$–AgBr system indicates the presence of a hypothetical unstable compound, practically all of which is dissociated at 449°.

3. Zinc, lead, and silver bromides are unlimitedly soluble in molten cadmium bromide.

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THE OXONIUM ION IN THE CRYSTAL LATTICES OF INORGANIC COMPOUNDS

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The oxonium ion won its citizenship rights as one of the constituents of aqueous solutions a long time ago. But the references in the literature to the role of this ion in the lattice structures of solid crystalline compounds are rather rare, being based almost exclusively upon X-ray data and referring to the crystalhydrates of some acids.

Vollmer [1], for instance, notes the striking resemblance between the X-ray photos of ammonium perchlorate NH_4ClO_4 and perchloric acid monohydrate $HClO_4 \cdot H_2O$. The position of nitrogen in the X-ray photo of ammonium perchlorate is occupied by oxygen in the X-ray photo of perchloric acid monohydrate. The author believes that the latter should, therefore, be regarded as an oxonium perchlorate, $OH_3 \cdot ClO_4$.

Zachariasen [2] made an X-ray analysis of oxalic acid dihydrate $H_2C_2O_4 \cdot 2H_2O$, and came to the conclusion that this compound should be regarded as an oxonium oxalate rather than as a hydrate of oxalic acid.

The data we have secured in our equilibrium investigations and comparisons of the crystalline forms of compounds provide new information on the participation of oxonium ions in the crystal lattice structure of inorganic compounds. These data support the conclusion that some salts, the empirical formulas of which include water, are actually oxonium compounds. Furthermore, these data represent a new contribution to our notions of the nature of the water that enters into the empirical formulas of mineral substances. They make it necessary to distinguish the so-called "oxonium" water from other types of chemically combined water and they provide a method for proving that water of this type is present in a compound.

The occasion for this research was our observation of the change that takes place in the composition of the anhydrous analogs of alums [3] when the composition of the solution from which these compounds are crystallized is changed. A large increase in the percentage of H_2SO_4 in the mother liquor from which $NH_4Al(SO_4)_2$ was crystallized reduced the precentage of ammonium in the resulting crystals while the percentages of aluminum and SO_4'' were nearly unchanged, as were the homogeneity and form of the crystals. It was natural to assume that increasing the percentage of H_2SO_4 would result in an isomorphic substitution of another ion for the NH_4^+ ion, and that this other ion, close to the latter in weight, would have a weight and structure quite close to that of the oxonium ion. The radium of the NH_4^+ ion is 1.43-1.44 Å [4]. According to the computations of

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Van Arkel, the radius of the oxonium ion is no more than 1.12 Å [5]. But, as Vollmer points out [1], we must expect the space requirements of the NH_4^+ and OH_3^+ ions to be nearly alike, since the difference between the volumes of the NH_3 and OH_2 ($NH_3 > OH_2$) must be balanced by the weaker bond existing between the H^+ and the OH_2. In fact, the atomic distances listed in Zachariasen's paper [2] cited above enable us to assume that the ionic radius of the oxonium ion is 1.35 Å in oxalic acid dihydrate. About the same value, namely 1.32 Å, is taken for the effective radius of this ion in Hassel's Crystal Chemistry, [6]. The pronounced analogy in the nature of the NH_4^+ and OH_3^+ ions and the available data justify us in assuming that the difference in the effective radii of these ions is small, and that, therefore, reciprocal isomorphic substitutions of these ions, resulting in the formation of mixed crystals, are quite probable.

We have made a study of the equilibrium in the quaternary system H_2O–SO_3–Fe_2O_3–$(NH_4)_2O$, in order to make a closer study of this problem as well as to disclose the genetic links between the anhydrous alums and the sulfates of the corresponding trivalent metals. This system has the advantage over the corresponding aluminum system of forming compounds of the $M^{+}M^{+++}(SO_4)_2''$ type at much lower temperatures and in much less highly concentrated solutions. The phenomena of ion exchange that interested us could be investigated at a temperature of no more than 100° in this system, which simplified our research procedure considerably. Of the material secured during this investigation we shall cite a portion that refers directly to the subject of the present paper.

If a gradually increasing percentage of ammonium sulfate is introduced into the ternary system H_2O–SO_3–Fe_2O_3 at $\underline{t}$ = 100° in the regions of crystallization of the acid ferric sulfate trihydrate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ and nonohydrate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, nearly all the added ammonium ions pass into the bottom phases until the latter are saturated with ammonium, thus converting the sulfates into anhydrous ammonium ferric alum.

In the light of Werner's theory ammonium ferric alum, $NH_4Fe(SO_4)_2$ should be regarded as a combination of the NH_4^+ ion with the univalent complex anion $[Fe(SO_4)_2]'$ [7]. We still do not possess direct experimental proof of the correctness of this approach to anhydrous alums. Weinland's attempt to use the conductance method developed by Werner and Miolatti for this purpose ended in failure. The salt was hydrated when it dissolved, and the conductance of the solution differed in no way from that of a solution of an ordinary alum. We do have indirect evidence, however, that this concept is correct. Thus, the comparison we have made of the changes in the conductance of acid solutions of iron and potash alums with temperature enable us to reach an as yet merely qualitative conclusion, to be sure, concerning the entrance of Fe^{+++} and SO_4^{--} ions into complex ions at high temperatures in solutions, from which crystals of an anhydrous alum are recovered when the temperature is raised still higher. But if the anhydrous alum represents a combination of the NH_4^+ and $[Fe(SO_4)_2]'$ ions, the ready conversion of the nonahydrated and trihydrated ferric sulfates into this compound, which takes place when ammonium ions are introduced into the H_2O–SO_3–Fe_2O_3 ternary system, gives us ground to assume that the same complex anion $[Fe(SO_4)_2]'$ underlies all these compounds, its combination with one cation or another resulting either in an anhydrous alum or in one of the ferric sulfates mentioned above.

The acid sulfate trihydrate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ is of particular interest with regard to the question of the isomorphism of OH_3^+ and NH_4^+ ions.

When acted upon by NH_4^+ ions, this sulfate is readily converted into the anhydrous alum $NH_4Fe(SO_4)_2$, as stated above, while the converse treatment of the anhydrous alum with sulfuric acid (using 4 volumes of H_2SO_4 to 1 volume of water) at $\underline{t}$ = 100° yields the trihydrated sulfate. The percentages of Fe^{+++} and SO_4^{--}

in the solid phase remain almost unaffected by these conversions, only the percentage of NH_4^+ being changed, (Table 1).

This justifies the assumption that the trihydrated sulfate is an oxonium compound of the anhydrous alum. In fact, the elementary composition of this sulfate matches the structural formula $OH_3^+[Fe(SO_4)_2]^-$, according to which this sulfate is an anhydrous alum in which the NH_4^+ ion or the ion of an alkali metal is replaced by the oxonium ion:

$$Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O = 2[OH_3^+][Fe(SO_4)_2]^-.$$

TABLE 1

Experiments on the Treatment of Anhydrous Ammonium Ferric Alum with Solutions of H_2SO_4 in Vessels Used to Determine Its Solubility at $t = 100°$.

Solid phase	Solution	Duration of treatment	Appearance of solid phase under the microscope	Composition of the solid phase			Remarks
				Fe_2O_3	SO_3	NH_4	
5 g of anhydrous alum, $NH_4Fe(SO_4)_2$			Hexagons	30.07	60.17	6.77	Original composition
	4 vol. H_2SO_4 1 vol. H_2O 25 ml	3 days	Minute grains and hexagons				
	Another 25 ml batch of solution	2 days	The same				
	Another 25 ml batch of solution	9 days	The same	29.17	59.2	1.09	Final composition

But if the trihydrated acid sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ is a combination of an oxonium ion with the $[Fe(SO_4)_2]^-$ anion, there is reason to believe that the nonahydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, which is formed when the relative percentage of water in the system is higher and whose region of crystallization abuts directly on the crystallization region of the trihydrate, and which (like the trihydrated sulfate) is converted into anhydrous ammonium ferric alum when ammonium ions are introduced into the system, is a combination of an oxonium ion hydrated by three molecules of water with the complex anion: $[OH_3 \cdot 3H_2O]^+[Fe(SO_4)_2]^-$, which is in agreement with its composition and with the circumstance that of the nine molecules of water in this sulfate, six can be recovered more easily than the remaining three and, hence, are molecular water.

The reason for our thinking that the crystallization water in the nonahydrated sulfate is linked to the oxonium ion is that the nonahydrated sulfate, like the trihydrated sulfate, is converted into an anhydrous alum containing the anhydrous anion $[Fe(SO_4)_2]^-$, when ammonium anions are introduced into the system. But, in view of the fact that the only way in which the nonahydrated sulfate can

be converted into the anhydrous alum is by recrystallization, we have no uncontestable proof of the assertion that all the molecules of crystallization water in crystals of the nonahydrated sulfate are coordinated about the oxonium ions. The only way in which the question of the arrangement of these molecules can be settled is by means of X-ray analysis of the crystals. That is why it is better to write the formula of the nonahydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ thus: $[OH_3]'[Fe(SO_4)_2]' \cdot 3H_2O$ leaving the question of the location of the molecular water open for the time being. Accordingly, the conversion of the sulfates into the anhydrous alum, at any rate the conversion of the trihydrated sulfate into the anhydrous alum, should be regarded as a process involving the replacement of the oxonium ions by ammonium ions:

$$OH_3^{\cdot}[Fe(SO_4)_2]' + NH_4^{\cdot} = NH_4^{\cdot}[Fe(SO_4)_2]' + OH_3^{\cdot}.$$

In view of the similarity of the nature and dimensions of the $OH_3^{\cdot}$ and $NH_4^{\cdot}$ ions, it was natural to assume that the conversion of the trihydrated sulfate might be an isomorphic substitution process. The available data in the literature on the crystalline form of these compounds does not support such a notion, however. Two crystalline forms are mentioned in the literature for iron acid sulfate trihydrate [8]. According to Scharitzer, this sulfate crystallizes as flat monoclinic crystals.

During their investigation of the equilibrium in the ternary H_2O-SO_3-Fe_2O_3 system, Posnjak and Merwin observed the formation of this sulfate as extremely minute needles, which could not be recovered from the solution in a sufficiently pure state to allow of their analysis, according to the authors, and could not be subjected to closer crystallographic investigation.

Both of these crystalline forms of the trihydrated sulfate mentioned in the literature differ from the form that is characteristic of the anhydrous alum. All authors have observed this compound in the shape of typical hexagonal platelets [9]; that is why the observation made by P.A.Martynov and the present author that the trihydrated sulfate can also be secured in the form of beautifully formed microscopic hexagonal platelets, like those in which the anhydrous alum crystallizes, was extremely valuable for our search.

Thus, when 10 g of acid ferric sulfate nonahydrate, 16 cm^3 of water, and 24 cm^3 of concentrated H_2SO_4 was placed in the usual vessel for studying salt equilibria, fitted with a mercury or an oil seal, and the system was stirred for several days at $\underline{t} = 100°$, the bottom phase, viewed under a microscope, was seen to consist of true hexagonal platelets, the composition of which was that of the trihydrated ferric sulfate.

By Analysis	Calculated
Fe_2O_3 29.85; SO_3 59.60.	Fe_2O_3 29.91; SO_3 59.98

Later on, after keepting the crystals, which contained 0.2-0.3% $NH_4^{\cdot}$, in their mother liquor in a sealed tube at $\underline{t} = 100°$ for several months, we secured hexagonal platelets that were large enough to enable us to establish the isotropism of a hexagonal section quite plainly when the crystals were examined in parallel polarized light, as well as the cross that is typical of the hexagonal system, which does not vary when the stage of the microscope is rotated during examination of the crystals in convergent polarized light. This similarity between the crystalline forms of the anhydrous alum and the acid ferric sulfate trihydrate, together with the similarity of their chemical formulas and the thoroughgoing analogy between the natures of the ions that replaced one another, provided rather weighty grounds for assuming that the foregoing conversion of one of these compounds into the other is a continuous process in which the $NH_4^{\cdot}$ and $OH_3^{\cdot}$ ions replace one another isomorphically. In fact, during the conversions of the trihydrated sulfate into the anhydrous alum and back again, examination of the solid

phase under the microscope during various stages of the process always showed that it was homogeneous throughout the mass. The latter consisted largely of extremely small crystalline grains, which apparently represented the minutest hexagonal platelets, sometimes easily distinguishable under the microscope.

The conversion of the nonahydrated sulfate into the anhydrous alum took an altogether different turn. This process does not involve an isomorphic substitution. As long as the number of ammonium ions introduced into the system is insufficient for complete transformation, the precipitate is heterogeneous. When it is examined microscopically, we find that it is a mixture of hexagonal platelets of the anhydrous alum and the typical rhombic crystals of the nonahydrated sulfate. Accordingly, the distribution of ions between the solid phases and the liquid solution corresponds to the presence of one solid phase of variable composition in equilibrium with the solution in the first instance, and of two such solid phases in the second, [10]. The data of Table 2 show that when small,

TABLE 2

Equilibria in the Crystallization Region of Ferric Acid Sulfate Trihydrate, $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$, at t = 100°
(Mean values of several experiments) Initial composition of the system: 10 g $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, 16 g H_2O, and 24 ml concentrated H_2SO_4

Quantity of $(NH_4)_2SO_4$ added, g	Number of tests*	Bottom phases				Liquid phases			Remarks
		NH_4^+	Fe^{+++}	SO_4''	OH_3^+	NH_4^+	Fe^{+++}	SO_4''	
0.01	3	0.157	19.147	68.88	6.94	0.0067	0.165	63.58	The tests were run in sealed ampoules, rotated for 7 to 22 days in an air thermostat
0.02	5	0.186	20.0	69.74	6.92	0.0079	–	65.40	
0.05	2	0.21	21.07	70.08	6.895	0.00825	0.134	63.00	
0.1	5	0.38	20.3	70.32	6.72	0.0121	–	64.88	
0.2	8	0.744	19.51	69.72	6.335	0.0136	–	65.72	
0.5	5	1.61	20.12	70.66	5.42	0.023	0.116	65.10	
0.7	4	2.39	19.94	70.20	4.58	0.0355	–	–	
1.0	4	3.35	20.07	70.32	–	0.0364	–	64.51	
1.2	3	3.8	19.51	70.32	3.12	0.043	0.071	–	
1.7	2	5.11	19.54	70.20	1.750	0.080	0.049	64.97	
2.5	4	5.95	19.94	70.37	0.859	0.28	0.025	62.83	

gradually increasing amounts of one of the cations – the NH_4^+ ion – are introduced into the system in the region of crystallization of the trihydrated acid sulfate, the percentage of this ion rises in both the liquid and the solid phases. Since the concentration of the second cation – the OH_3^+ ion – in the solution remains approximately constant, the uninterrupted rise of the percentage of NH_4^+ in the solution indicates that a single solid phase of variable composition is in equilibrium with the solution.

When, under the same conditions, the percentage of NH_4^+ in the precipitate increases in the crystallization region of the nonahydrated sulfate, the percentage of NH_4^+ in the solution remains approximately constant (Table 3).

We secured interesting figures on the isomorphism phenomena when we investigated the equilibrium in the region of crystallization of ferric acid sulfate nonohydrate $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. Athanasesco [11] produced this sulfate by heating a 25% solution of ferric sulfate to 150°. Posnjak and Merwin [12] describe it as one of the equilibrium phases in the H_2O–SO_3–Fe_2O_3 system, which is stable when in contact with solutions of certain compositions at temperatures ranging from room temperature to 170°. We prepared this sulfate by heating 15%–20% solutions of neutral ferric sulfate to 160-170° in an autoclave for 3 hours. The precipitates

*Averaged.

TABLE 3

Equilibria in the Crystallization Region of the Nonahydrated Acid Sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ at t = 100°

Initial composition of the system: 10 g $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, 13 g H_2O, 17 ml H_2SO_4, conc.

Quantity of $(NH_4)_2SO_4$ added, g	Bottom phases			Liquid phases			Remarks
	NH_4'	$Fe^{...}$	SO_4''	NH_4'	$Fe^{...}$	SO_4''	
0.2	0.55	–	59.5	0.045	0.31	55.5	The experiments were conducted in vessels usually employed for studying equilibria. The experiments lasted 7 to 22 days.
0.5	1.6	17.4	63.2	0.037	0.28	55.6	
1.0	3.13	–	–	0.036	–	–	
1.5	5.0	–	–	0.04	–	–	

were yellow powders of various shades, ranging to a dark yellow, nearly brown color. Under the microscope they were rhombohedra, very close to a cube in shape.

The composition of this sulfate and the conditions of its formation make the four following ionic formulas all possible ones for it:

1) $Fe_3^{...}(SO_4)_2''(OH)_5'(H_2O)_2$; 2) $Fe_3^{...}(SO_4)_2''(OH)_8' \cdot OH_3^{\cdot}$;

3) $Fe_3^{...}(SO_4)_2''(OH)_8'H^{\cdot}H_2O$; 4) $Fe_3^{...}(SO_4)_2''(OH)_7' \cdot H_2^{\cdot}$.

Under similar conditions we prepared the ammonium derivative of this sulfate, $3Fe_2O_3 \cdot 4SO_3 \cdot (NH_4)_2O \cdot 9H_2O$, which can have only the following ionic formula, according to its composition and the nature of the medium from which it was isolated:

5) $Fe_3^{...}(SO_4)_2''(OH)_8'NH_4^{\cdot}$.

We prepared this compound as a lamellar, scablike, brown precipitate by heating 20-25 ml of a solution containing 0.03 mol of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ + 0.05 mol of H_2SO_4 in 100 ml of water to 170° for 2 hours in a sealed tube. Analysis of this salt yielded the following results.

By analysis			Calculated		
$Fe^{...}$	$NH_4^{\cdot}$	SO_4''	$Fe^{...}$	$NH_4^{\cdot}$	SO_4''
35.3	3.6	40.5	34.9	3.76	40.05
35.11	3.6	40.6			

Microscopic examination showed it to consist of rhombohedra. The salt dissolved extremely slowly when heated in a concentrated solution of hydrochloric acid. We also obtained this salt as one of the phases in the quaternary equilibrium system H_2O–SO_3–Fe_2O_3–$(NH_4)_2O$, by introducing NH_4 ions into the ternary H_2O–SO_3–Fe_2O_3 system in the region of crystallization of the nonahydrated basic sulfate. This converted the basic sulfate into its ammonium derivative (Table 4).

When we compare these formulas, it is readily seen that Formula (5), which is the only possible one for the ammonium derivative, is derived from Formula (2), by substituting the ammonium ion for the oxonium ion in it. This enables us to select Formula (2) of the four formulas listed and to regard the basic sulfate $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ as an oxonium salt.

When small, gradually increasing, quantities of $NH_4^{\cdot}$ ions are added to the H_2O–SO_3–Fe_2O_3 ternary system in the crystallization region of this sulfate, the latter is converted, as we have said, into its ammonium derivative. The percentage of $Fe^{...}$ and SO_4'' in the solid phase remains almost constant, as in the trihydrated acid sulfate, while the percentage of $NH_4^{\cdot}$ increases in the solid as well

as liquid phases. Together with the homogeneity of the precipitate, this is evidence that the solution is in equilibrium with a single solid phase of variable composition – mixed crystals of the nonahydrated basic sulfate and its ammonium derivative, the process of conversion:

$$3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O \rightarrow 3Fe_2O_3 \cdot 4SO_3(NH_4)_2O \cdot 6H_2O,$$

constituting a continuous process, in which the OH_3^+ ions are replaced by the isomorphic NH_4^+ ions. The data on these experiments are listed in Table 4.

TABLE 4

Equilibria in the Crystallization of the Nonahydrated Basic Sulfate $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ at $t = 100°$*

Initial composition of the system: 10 g $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, 20 ml H_2O, and 1 ml concentrated H_2SO_4

Quantity of $(NH_4)_2SO_4$ added, g	Solid phase			Liquid phase			Remarks
	NH_4'	$Fe^{\cdot\cdot\cdot}$	SO_4''	NH_4'	$Fe^{\cdot\cdot\cdot}$	SO_4''	
0	0	35.32	42.7	0	5.46	13.39	The tests were run in sealed ampoules, rotated for 20 to 30 days in an air thermostat.
0	0	35.63	40.67	0	5.88	14.05	
0.1	0.57	36.69	38.42	0.016	5.7	14.73	
0.1	0.55	35.44	40.48	–	–	14.0	
0.25	1.27	36.5	39.7	0.029	5.29	14.2	
0.5	2.77	34.97	40.2	0.051	–	–	
0.75	3.3	35.73	40.42	0.068	4.6	14.28	
1.0	3.49	35.0	40.0	0.088	4.04	–	

Accordingly, the structural formulas for this sulfate and its ammonium derivative are as follows:

$$\left[\begin{matrix} Fe(OH)_2 \\ \diagup\!\diagdown SO_4 \\ Fe(OH)_2 \\ \diagup\!\diagdown SO_4 \\ Fe(OH)_2 \end{matrix}\right] OH_3^+ \quad \text{and} \quad \left[\begin{matrix} Fe(OH)_2 \\ \diagup\!\diagdown SO_4 \\ Fe(OH)_2 \\ \diagup\!\diagdown SO_4 \\ Fe(OH)_2 \end{matrix}\right] NH_4^+$$

The fact that the basic salt is an oxonium compound is highly interesting. The second of these salts, which we synthesized artificially, was a so-called "ammoniojarosite," a representative of the jarosite group of minerals. We get the most important of these minerals – the potassium jarosite – by substituting the potassium ion for the OH_3^+ or NH_4^+ ion in the formulas cited.

The farreaching analogy between the crystallographic properties of the nonahydrated basic sulfate and those of minerals of the alunite-jarosite group has been commented on by other researchers [12].

The reason behind this analogy remained obscure, however. This analogy is thoroughly explained by what has been set forth above.

The minerals of the jarosite group can be derived from this basic sulfate by means of isomorphic replacement of the oxonium ion by ions of NH_4^+, K^+, and other metals of the alkali group.

These concepts of the structure of the jarosites and of basic ferric sulfate nonahydrate are in conformity with the data of the X-ray analysis of these com-

*In collaboration with E. A. Krogius and with the assistance of A. E. Gavrikova.

pounds cited in the paper by the American researchers Sterling and Hendricks [13]. According to them, the structure of $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ is practically identical with that of the jarosites, the place of potassium in the jarosite lattice being occupied by oxygen in the $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ lattice. Still, the authors themselves interpret the analysis results incorrectly. They assume that the transition from the jarosites to $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ occurs as the result of an isomorphic substitution of a molecule of water for the K^+ ion, accompanied by the conversion of one of the hydroxyl groups into H_2O. They represent the potassium jaorsite and the nonahydrated basic sulfate accordingly by the following formulas:

$KFe(SO_4)_2(OH)_5(OH)$; $H_2O \cdot Fe_3(SO_4)_2(OH)_5 \cdot H_2O$.

As we see it, these compounds ought to be represented by the following formulas: 1. $KFe_3(SO_4)_2(OH)_6$; 2. $OH_3Fe_3(SO_4)_2(OH)_6$.

The material set forth in the present paper entitles us to think that oxonium ions are a frequent structural element of the lattices of inorganic compounds that are formed from aqueous solutions. In the instances we have investigated, these ions were found to be replaceable by ammonium ions and ions of alkali metals, and it must be supposed that the method of ion substitution we have employed, especially the method of preparing ammonium derivatives, will be used to detect these ions in various compounds.

One of the consequences of the results we have obtained is the necessity for a rexamination and a refining of current concepts in the chemistry of minerals on so-called "water of constitution," the necessity for making a distinction between the so-called "oxonium water" and other kinds of water of constitution in the elementary formulas of minerals. Apparently, the three molecules of water in the empirical formulas of inorganic compounds, which represent them as a combination of basic and acid oxides and water, often constitute the hypothetical oxonium oxide $(OH_3)_2O$, similar to the hypothetical ammonium oxide $(NH_4)_2O$ and based on the oxonium ions that actually exist in the substance. The existence of compounds whose crystalline forms are similar and whose empirical formulas differ in that the three molecules of water in one of these compounds are replaced by an oxide of an alkali metal or an oxide of ammonium in the other compound, justifies our assuming that the three molecules of water in the first compound constitute the hypothetical oxonium oxide, and that the place of the alkali-metal or ammonium ions in this compound is therefore occupied by oxonium ions.* Determining the presence of this kind of water in compounds by means of the outlined comparison of their compositions or by the substitution method described above can aid in understanding their nature, as was shown above in the case of the ferric sulfates.

The difficulties involved in setting up the structural formulas of inorganic compounds and of minerals, in particular, are largely related to the presence of water in their empirical formulas. This bears out the importance of discriminating between them and of classifying them according to their varieties.

Scharitzer's resume in Doelter and Leitmeier [14] cites the constitutional formulas for aqueous ferric sulfates proposed by various research workers. Most of these formulas hardly reproduce the actual structure of the minerals. The reasons for this are, on the one hand, the fact that the authors derive their conclusions regarding the structure of these compounds from a consideration of the compounds by themselves, unrelated to the medium in which they are formed, and, on the other, the inadequacy of contemporary notions of the nature of the water in minerals.

By way of example, we may cite the formula for rhomboclase, which is identical with the nonahydrated acid ferric sulfate we have discussed earlier. The

*The conversion is not always true. Thus in $H_2C_2O_4 \cdot 2H_2O$ the OH_3 ions apparently cannot be replaced isomorphically by NH_4^+ ions.

survey cited the formulas given for this compound by Recourt, Weinland, and Ensgraber, and the author of the survey himself.

All these formulas differ from the above-cited formula for this compound proposed by us:

$$OH_3 \cdot [Fe(SO_4)_2]' 3H_2O.$$

Of all the formulas cited in Scharitzer's survey for this sulfate, the least successful is the formula put forward by the survey's author:

$$HO\text{-}Fe\begin{matrix} SO_4H \\ \\ SO_4H \end{matrix} + 3H_2O.$$

According to this formula, rhomboclase is a hydroxo derivative, which does not accord at all with the conditions under which this compound is formed in the H_2O–SO_3–Fe_2O_3 system.

In conformity with what has been set forth above, we may put forward the following more accurate classification of water in the empirical formulas for minerals, which differs from the one generally accepted at the present time.

I. The water that enters into the composition of the substance as independent molecules and can be recovered from the minerals rather readily should be called molecular water, two well-known and generally accepted subgroups being distinguished:

a) Water of hydration or of crystallization, part of the constitution of certain hydrates and entering into the composition of the substance in rigorously definite stoichiometrical proportions.

b) Zeolitic or dissolved water.

II. Water that is harder to separate out and usually is recovered together with other constituents, the so-called water of constitution, the elements of which do not exist in the crystal lattice as molecules of water but enter into the formation of various ions, should be called ionic water and divided into three subgroups:

a) Hydroxyl water, the elements of which are used in the construction of hydroxyl ions.

b) Oxonium water, which is used in the formation of oxonium ions, each three molecules of such water constituting the hypothetical oxonium oxide, $(OH_3)_2O$;

c) The water of protonoacidic coordination compounds.

According to the foregoing, the three molecules of water in the empirical formula for the trihydrated acid sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ represent ionic (or constitutional) water, namely, oxonium water: $Fe_2O_3 \cdot 4SO_3 \cdot (H_3O)_2O$.

Of the nine molecules of water in the empirical formula for the nonahydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, three molecules are ionic (constitutional) water, namely, oxonium water, while the other six are molecular – water of crystallization or hydration: $Fe_2O_3 \cdot 4SO_3 (H_3O)_2 (6H_2O)$ molecular.

Indeed, the data of both Recourt and Scharitzer indicate that six of the nine molecules of water in rhomboclase can be separated much more readily than the other three.

In the nonahydrated basic sulfate $3Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, all the nine molecules are ionic water. Three of them are oxonium water, while the other six are hydroxyl water:

$$3Fe_2O_3 \cdot 4SO_3 \cdot (H_3O)_2O \cdot (6H_2O)_{hydroxyl}.$$

SUMMARY

1. New instances of the participation of oxonium ions in the construction of the crystal lattices of inorganic compounds have been described. The data secured in a study of equilibria and from a comparison of the crystalline forms of the compounds demonstrate that some salts, the empirical formulas of which contain water, should be regarded as oxonium compounds.

2. The existence of a new crystalline form of acid ferric sulfate trihydrate, $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$, hitherto unknown in the literature, which is of some importance for the problem of the isomorphism of $OH_3^\cdot$ and $NH_4^\cdot$ ions, has been established.

3. Structural formulas have been derived for the acid ferric sulfates $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ and $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$. The similarity of type of the chemical formulas and the analogy between the crystalline forms of the trihydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ and the anhydrous alum have been established.

It has been shown that the $OH_3^\cdot$ and $NH_4^\cdot$ ions replace each other isomorphically when the trihydrated sulfate is converted into the anhydrous alum and vice versa.

4. An isomorphic ammonium derivative of the nonahydrated basic sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, the composition and crystalline form of which are that of minerals of the jarosite group, has been prepared. The composition of this ammonium derivative agrees with the empirical formula $3Fe_2O_3 \cdot 4SO_3 \cdot (NH_4)_2O \cdot 6H_2O$.

5. The structural formulas of the nonahydrated basic sulfate and its ammonium derivative are given. It is shown that this sulfate is an oxonium derivative of minerals of the jarosite group.

It is shown that the $OH_3^\cdot$ and $NH_4^\cdot$ ions replace each other isomorphically when this sulfate is converted into its ammonium derivative.

6. The necessity of distinguishing so-called "oxonium" water as one of the kinds of water of constitution is pointed out, and the significance of the latter for a correct understanding of the structure of mineral substances is noted.

A method is set forth that makes it possible to establish the presence of oxonium water in a compound.

7. A new and improved classification of the varieties of water in the empirical formulas of mineral substances is proposed.

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KINETIC INVESTIGATIONS OF THE DECOMPOSITION OF SILVER OXIDE

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The decomposition of silver oxide is one of the reactions that involve the disintegration and formation of the crystal lattice. Therefore a study of the mechanism involved in the decomposition of this substance may contribute considerably to an understanding of the mechanism of other reactions in the same class. A characteristic feature of most such decomposition reactions is the rise in the reaction rate with time. The reason for this acceleration of the reaction is supposed to be the solid reaction product. According to Vollmer [1], the presence of the latter facilitates the crystallization process, i.e., the conversion of the substance from a gaseous state to a solid. As Roginsky [3] has shown, the kinetic equation for the growth of the crystal depends upon whether nuclei are formed at the faces, edges, or polyhedral angles. According to Schwab [2], a solid reaction product exerts a catalytic action upon the decomposition of solid substances. Hence, the activation energy of a given reaction should vary, depending upon whether it takes place with or without a solid end product present.

Lewis [5] established that adding silver, manganese dioxide, and platinum to the initial product in the reaction we are discussing speeds up the decomposition of the silver oxide. As Lewis points out, these substances tend to accelerate the recombination of the oxygen atoms liberated during decomposition.

According to Vollmer, these products accelerate the conversion of the silver evolved from the gaseous state to the crystalline state, thus accelerating the decomposition reaction; according to Schwab, these products deform the molecules located at the boundary between the initial product and the catalyst, which lowers the activation energy.

Thus, the views of the role of the solid product in this as well as in other reactions differ. And yet, this problem is fundamental in the study of the mechanism of reactions. The author has expressed the supposition that autoacceleration of a reaction may also take place when the solid product does not exert any catalytic effect [5]. In the present paper we propose to investigate the effect of silver upon the rate of decomposition of its oxide, both by adding silver to the initial product and by removing the silver formed as the result of the reaction.

EXPERIMENTAL

The initial product – silver oxide – was produced by precipitating silver nitrate that had been recrystallized twice with caustic potash at room temperature. After precipitation, the precipitate was repeatedly washed with distilled water, then desiccated at 55° in a drying cabinet, and finally dried out under vacuum at room temperature. Since silver oxide is sensitive to light, it was prepared in red light. The product was stored in the dark. The reaction was performed in a vessel that was blackened on the outside.

The decomposition reaction rate was determined by the change in the pressure of the liberated oxygen per unit time. The pressure was measured by a mercury

manometer soldered to the apparatus. 0.2 g of silver oxide was placed in the reaction vessel, which was then connected to the apparatus by means of a ground-glass connection. The air was pumped out of the apparatus by means of a vacuum pump until the pressure was 0.1 mm. The silver oxide was kept under vacuum while exhaustion was continued for 5-10 minutes; then the reaction vessel was placed in a thermostat, the temperature of which was controlled within 0.1° up to 170° and within 0.5° above 170°.

The decomposition of 0.2 g of silver oxide ought to liberate 9.7 ml of oxygen at 760 mm and 0°. The volume occupied by the liberated oxygen in the apparatus was 75 ml. The maximum pressure of oxygen when all the silver oxide is decomposed ought to be 104.6 mm at room temperature (18°). A pressure lower than that indicates the incomplete decomposition of the initial product. The tests were run at temperatures ranging from 118 to 222°. The results of the tests run at 118, 150, 160, and 170° are represented by Curves 1, 2, 3, and 4 in Fig. 1. We see from these curves that in every case the velocity of the reaction is highest at the beginning, then falling away to zero at the temperatures 118 and 150°, and passing through a slight maximum at the temperatures 160 and 170°. The higher the temperature, the more pronounced is the maximum on the decomposition curve. At these temperatures, the pressure of the liberated oxygen is 10, 35, 45, and 87 mm, repsectively, or 9.5, 33.5, 43, and 83 per cent decomposition of the silver bromide. After a certain interval of time has elapsed, the pressure in the system hardly changed at all, and the decomposition rate was zero. It seems to us that the appearance of a maximum on the curves was due to the fact that the initial product consisted of at least two different sizes of particles that were quite different. The small particles decompose at the very start at the maximum rate, while the rate is zero for the large ones. As time goes on, the decomposition rate of the small particles decreases, while that of the large ones rises. Eliminating the large particles or carefully pulverizing the initial product ought to result in an increase in the rate of reaction, with the maximum disappearing.

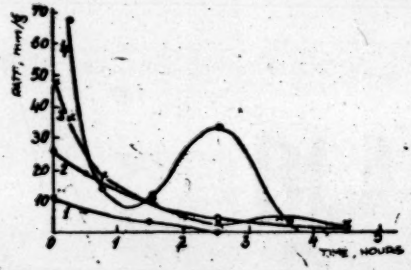

Fig. 1.

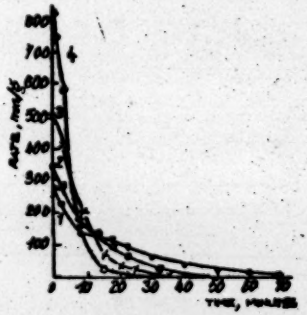

Fig. 2.

Curves 1, 2, 3, and 4 of Fig. 2 reproduce the results of tests run at 172, 180, 204, and 222° C with a silver oxide that had been carefully pulverized in a mortar. At none of these temperatures did the carefully pulverized silver oxide exhibit a maximum on the rate-time curves of its decomposition. The reaction rate at the start of the reaction was 3 to 4 times higher for the pulverized product than for the product that was not pulverized.

At low temperatures, up to about 180°, silver oxide does not decompose completely. Above this temperature the amount of oxygen evolved was practically equal to the amount of oxygen in the weighed portion of the initial product. The temperature coefficient of the reaction, computed from the initial reaction rates in the 180-222° range, was 1.26.

Mixing silver oxide with powdered silver, obtained by decomposing the oxide, did not change the reaction rate. Nor was the rate of decomposition affected by mixing the silver oxide with cupric oxide. We were most interested, however, in learning the effect of adding mercury upon the rate of decomposition. As we know, silver forms an amalgam with mercury readily. The presence of the latter in the reaction vessel during the reaction ought to result in the vanishing of the reactinn product – silver – from the solid phase and the formation of an amalgam. The boundary between Ag_2O_{solid} and Ag_{solid} should vanish, being replaced by a new boundary: Ag_2O_{solid}–amalgam. The solid reaction product – silver – can be removed completely by treating the partially decomposed silver oxide carefully with mercury. Continuing this test therefore enables one to determine the effect of the boundary and of the solid end product upon the reaction rate.

The experiments on the effect of mercury upon the reaction rate were conducted as follows. From 0.2 to 0.8 g of mercury was added to a weighed quantity of silver oxide, placed in the reaction vessel. The contents were agitated for a few minutes, after which decomposition was effected at various temperatures (160 to 220°). Here, too, the reaction set in with the maximum velocity, subsequently dropping off to zero. In all these tests the initial reaction rate was several times higher than when no mercury was present. The quantity of oxygen evolved at the temperature at which the silver oxide was fully decomposed corresponded to the amount of oxygen in the weighed sample; this indicated that the mercury is not oxidized by the oxygen evolved during decomposition in the temperature range we investigated. In some of the tests, the silver oxide was agitated with the mercury for a few minutes after which the oxide was mechanically separated from the mercury and decomposed. Here, too, the initial reaction rate was more than 2 times as high as the rate of decomposition without mercury. In all cases, the rate of decomposition with mercury present was higher than when no mercury was present, throughout the temperature range, 160-220°, of our investigations.

The experiments run at 180° and higher, with 0.4 g of silver oxide in an oxygen atmosphere the initial pressure of which was 427 mm, indicated that the reverse reaction, i.e., the formation of Ag_2O from Ag and O_2 was unimportant. The amount of oxygen evolved in both cases corresponded to the amount of oxygen in the sample, although the oxygen pressure within the system greatly exceeded the pressure produced when the 0.2 g sample was decomposed in vacuum.

Evaluation of Results

The decomposition of silver oxide, which we have investigated, differs both in the shape of its kinetic curves and in its rate from the same reaction as studied by Lewis. According to Lewis, the reaction set in with zero velocity and obeyed the equation:

$$\frac{dx}{dt} = kx(1 - x),$$

where x is the quantity of reacted substance.

The quantity of oxygen liberated per unit time, at the maximum of 330° in Lewis's experiments, was about the same as at the start at 180° in our experiments. Before the maximum was reached half of the initial substance had decomposed. The rate of decomposition of his preparation at 180° can be calculated from the temperature coefficient of the reaction (1.5) observed by Lewis and the activation energy computed by us. The computation indicates that the rate of reaction at 180° at the maximum for Lewis' preparations must be 10^5 times

smaller than the initial decomposition rate of our preparations. Inasmuch as the order of magnitude of the reaction surface at the reaction maximum is the same as that of the crystal surface, the crystal surface of our preparations must have been about 10^5 as great as that of Lewis' preparation, for the same activation energy.

The activation energy of the decomposition of Ag_2O calculated by us from the temperature coefficient of the reaction as observed by Lewis, is 31.800 cal. The activation energy of the decomposition of our preparations of silver oxide, calculated from the temperature coefficient of the reaction (1.26) is 10,500 cal. The two preparations differ, we see, in their activation energies as well as in the degree of dispersion of the powder. The high initial rate of reaction may be ascribed either to the fact that practically the entire surface of the crystals is covered with nuclei of the reaction product at the very start, or to the fact that the molecules of silver oxide located at the surface of the crystals have the same reactivity and decompose with the same probability.

If silver nuclei are present in the oxide, the repeated treatment of the initial product with mercury before the experiment should have resulted in the complete extirpation of the nuclei owing to the dissolution of the silver in the mercury, and, hence, to a reduction of the rate of reaction at the start of the latter. Likewise, the decomposition of the oxide in the presence of liquid mercury ought to have resulted in a considerable decrease in the number of silver nuclei formed, and, hence, to a decrease in the reaction rate. In both instances not only did the reaction rate not decrease, but it increased. We thus have to assume that the maximum rate of decomposition observed at the start of the reaction is due to the identical reactivity of the particles at the surface of the powder.

An X-ray analysis, performed by Lazarev, senior scientific associate of the Institute of Chemistry of the Belorussian Academy of Sciences, demonstrated that our preparation of silver nitrate was an amorphous powder with a slight trace of the crystalline oxide. The X-ray photo of the silver oxide is shown in Fig. 3. (See Plate, page 665). Rings are hardly noticeable after an exposure of 12 hours, whereas intensive rings are visible in copper oxide after an exposure of 6 hours. The labile state and the irregular arrangement of the molecules in the amorphous powder are evidently the reason for the low value of the activation energy measured by us, as well as for the fact that the reaction sets in with maximum velocity. The presence of slight amounts of the crystalline oxide in the initial product results in the formation of a maximum toward the end of the reaction as the oxide is decomposed.

The increase in the reaction rate when mercury is present is due to the positive affinity between mercury and silver, which facilitates the process of decomposition.

Like Lewis, we believe that the decomposition of silver oxide involves the formation of atomic oxygen. As Lewis sees it, the catalysts he investigated accelerate the recombination of the oxygen atoms. Vollmer, discussing this same reaction, asserts that the catalysts accelerate the transition of the gaseous silver formed as the oxide molecules decompose, into the solid state. In both instances, the action of the catalysts results in reducing the velocity of the reverse reaction.

The overall process involved in the decomposition of silver oxide consists of a series of elementary processes. The heat of reaction can be computed for each of them.

Let us assume that the reaction proceeds as follows:

$$1)\ Ag_2O_{sol.} \longrightarrow 2Ag_{gas} + O - 200.8 \text{ cal.};$$

$$2)\ 2Ag_{gas} \longrightarrow 2Ag_{sol.} + 136 \text{ cal.};$$

3) $Ag_2O_{sol.} + O \rightarrow 2\,Ag_{gas} + O_2 - 16$ cal;

4) $2Ag_{sol.} + O \rightarrow Ag_2O_{gas} - ?$;

5) $O + O \rightarrow O_2 + 117$ cal.

In calculating the heats of reaction we took the heat of formation of silver oxide to be 6.3 Cal and the heat of sublimation of silver to be 68 Cal. As we see from the foregoing equations, it is impossible from the energy standpoint for gaseous silver and atomic oxygen to be formed by the direct decomposition of the molecule. The activation energy would have to be at least 200.8 Cal; the activation energy observed experimentally was much less.

The heats of reaction of Processes (2) and (5) can, of course, not be utilized to activate the first reaction: first, because they take place somewhat later, and second, because they take place in a different phase. Inasmuch as the subsequent reactions cannot occur unless the first one does, the proposed outline of the elementary processes is in need of improvement. The silver and oxygen atoms that are formed when the molecule breaks down do not enter the gaseous phase, but remain in an adsorbed state, occupying the place they occupied before the breakdown of the molecule. Then the energy of adsorption of 2 atoms of silver and 1 atom of oxygen will have to be subtracted from the energy required for decomposition. If we assume that the velocity of the overall process is governed by the rate of decomposition of the Ag_2O molecule and take the activation energy to be 10.5 Cal - equal to the heat of reaction required for decomposition:

$$6)\ Ag_2O_{solid} \rightarrow 2Ag_{adsorbed} + O_{adsorbed} - 200.8 + y,$$

the mean heat of adsorption will be 63.5 Cal per gram atom. Oxygen and silver atoms are held very firmly in the crystal lattice, so that it is quite unlikely that these atoms passed into the gaseous phase upon decomposition.

When the next molecules of silver oxide, lying directly alongside the adsorbed atoms of silver and oxygen, decompose, the adsorbed silver atoms interact with each other, as do the oxygen atoms. As the number of adsorbed silver atoms increases, the linkages between them increase, the linkages between these atoms and the oxide diminishing. When the two-dimensional space contains enough silver atoms, they form nuclei and continue to grow.

Thus, the second stage of the process is the formation of crystals of adsorbed silver atoms and the recombination of the adsorbed oxygen atoms. The two processes:

$$7)\ 2Ag_{adsorbed} + O_{adsorbed} \rightarrow 2Ag_{solid} + \frac{1}{2}\ O_2,$$

involve the evolution of 4.2 Cal of heat. Reaction (7) is paralleled by a reaction involving the formation of the oxide:

$$2Ag_{adsorbed} + O_{adsorbed} \rightarrow Ag_2O_{solid} + 10.5\ \text{Cal.}$$

and a reduction reaction:

$$Ag_2O_{solid} + O_{adsorbed} \rightarrow 2Ag_{adsorbed} + O_2.$$

The heat of reaction cannot be computed for this reaction, since we do not know the separate heats of adsorption of the oxygen and silver atoms. If we assume they are the same, the heat of reaction will be 47.5 Cal. Thus the reaction involves the liberation of heat.

SUMMARY

1. A study has been made of the rate of decomposition of silver oxide in the temperature range of 118-222°. In every case, the decomposition reaction was a

maximum at the very start.

2. X-ray analyses have shown that our preparation of silver oxide was an amorphous powder with small traces of the crystalline salt.

3. The activation energy of decomposition is 10.5 Cal.

4. It has been found that mercury accelerates the decomposition of silver oxide considerably.

5. The possible elementary processes have been examined, and it has been shown that the decomposition of the oxide must involve the formation of adsorbed atoms of oxygen and silver. This makes it impossible for any detectable supersaturation of silver to occur in the gaseous phase.

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AN INVESTIGATION OF THE COORDINATION COMPOUNDS OF PHOSPHOROUS PENTACHLORIDE AND PENTABROMIDE WITH IODINE CHLORIDE AND BROMIDE *

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In our previous reports [1,2,3] we have shown that chemical interaction between the components of the PX_5–I_2 and PX_3–IX** systems results in the formation of the same coordination compound, PX_4I. The formation of these coordination compounds may be represented by means of the following equations:

1. $PX_5 + I_2 \rightleftarrows PX_3 + 2IX$
   $2PX_5 + 2IX = 2PX_4I$
   $3PX_5 + I_2 = PX_3 + 2PX_4I$

2. $PX_3 + 2IX \rightleftarrows PX_5 + I_2$
   $PX_5 + IX = PX_4I$
   $PX_3 + 3IX + PX_4I + I_2$

As these reactions indicate, the foregoing systems PX_5–I_2 and PX_3–IX are transformed into the system PX_5–IX, which results in the formation of compounds with the formula PX_4I (i.e., PCl_4I or PBr_4I).

The present paper reports on an investigation of the PCl_5 – ICl systems by the thermal analysis and conductance methods. We also determined the conductance of the PCl_4I and PBr_4I coordination compounds in some nonaqueous solutions and made some cryoscopic determinations.

PBr_5–IBr System.*** This system was analyzed thermally at concentrations ranging up to 57.6 mol.% PBr_5. A eutectic point was found on the fusibility curve at 10.44 mol.% PBr_5 and 22.2°. The fusibility curve rises sharply as more PBr_5 is added, reaching a maximum at 50.14 mol.% PBr_5, which is evidence of the existence of a compound of the composition $PBr_5 \cdot IBr$ and a melting point of 114.6°. The maximum is followed by a flat section, due to the limited solubility of PBr_4I in PBr_5.

If PBr_5 is taken as the initial substance, which is melted and to which IBr is added, yellow crystals (PBr_5) can be seen on the walls of the vessel after the melt has cooled. As IBr is added, the quantity of PBr_5 diminishes, and the melt takes on the color that is characteristic of PBr_4I. The PBr_4I partially sublimes on the walls of the vessel as minute dark crimson needles.

The results of the thermal analysis are given in Table 1 and Fig. 1.

The specific conductance of the PBr_5–IBr system was measured at concentrations ranging from 0 to 23 mol.% PBr_5 at 45 and 55°. It was extremely difficult to measure the conductance of this system at high PBr_5 concentrations, since these measurements have to be made at much higher temperatures (100°) in order to have the system molten (Table 1) throughout the concentration range. Investigation of the PBr_5–IBr system, beginning with small PBr_5 concentrations, was impossible at such

* Report 8 of a series dealing with the physicochemical investigation of iodine solutions.

** X - chlorine or bromine, respectively.

*** The preparation and refining of the preparations have been described in a previous report [1].

TABLE 1

Thermal Analysis of the PBr_5 – IBr System

Mol. % PBr_5	Arrest points	Mol.% PBr_5	Arrest points
IBr	40.3	32.65	95.7
1.03	38.7	36.31	101.2
3.19	36.4	42.23	108.8
6.70	28.3	43.59	110.8
10.44	22.2	48.44	113.6
13.82	35.4	50.14	114.6
14.09	34.3	52.05	114.4
20.46	44.5	54.81	114.4
27.60	86.3	57.56	114.4

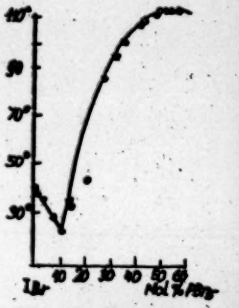

Fig. 1. Thermal analysis of the PBr_5 – IBr system.

temperatures owing to the thermal dissociation of the iodine bromide.

To get an idea of the conductance of the coordination compound PBr_5I, we prepared a melt containing 51.1 mol.% PBr_5, (i.e., very close to the composition of $PBr_5 \cdot IBr$) and measured its conductivity at four temperatures: 20, * 110,** 120, and 130°. The results of all these measurements are given in Tables 2 and 3 and shown in Fig. 2. They testify that the coordination compound PBr_5I (or $[PBr_4][IBr_2]$) is a rather strong electrolyte, possessing

Fig. 2. Specific conductance of the PBr_5–IBr system.

TABLE 2

Specific conductance of the PBr_5–IBr System

Mol.% PBr_5	Specific conductance, $\kappa \cdot 10^2$	
	45°	55°
IBr	0.084	0.080
3.80	2.5	2.9
6.64	3.4	3.8
9.82	3.4	3.8
13.17	3.0	3.6
16.42	2.4	2.9
19.30	2.0	2.4
22.75	1.5	1.9

TABLE 3

Specific Conductance of a Melt Containing 51.1 Mol.% PBr_5

Temp.	20°	110°	120°	130°
° κ	$2.4 \cdot 10^{-5}$	$3.8 \cdot 10^{-2}$	$4.7 \cdot 10^{-2}$	$5.1 \cdot 10^{-2}$

a conductivity of the order of 10^{-2} ohm^{-1} cm^{-1} in the molten state. At 45-55° the specific conductance of the PBr_5–IBr system first rises as the concentration of PBr_5 is increased, reaching a maximum value of $3\text{-}3.8 \cdot 10^{-2}$ ohm^{-1} cm^{-1} at 6-10 mol.% PBr_5, after which it drops off.

PCl_5–ICl System. The thermal analysis of the PCl_5–ICl system involves considerable difficulty, due in part to the great difference between the melting points of its two components – ICl melts at 27.1°, while PCl_5 melts at 162° (under pressure, with partial sublimation). At low PCl_5 concentrations – up to 10 mol.% –

* The conductivity of the solidified melt was measured.

** The conductivity of the slightly supercooled melt was measured.

the arrest points are sharply marked, without any supercooling.

A eutectic point was found to exist at 9.21 mol.% PCl_5 at 9.6°, the fusibility curve rising sharply beyond that point. The melt crystallizes with considerable supercooling and retardation. A flat crystallization plateau is rare, the melt crystallizing most often without any arrest point, but with a slight retardation of the drop in temperature.

It is difficult to make a thermal analysis at temperatures in excess of 80-90° owing to the partial decomposition of the iodine chloride. The mass has not yet melted when the ICl that is present in excess begins to decompose. To avoid the effects of high temperature, at which the ICl is partially decomposed, we determined the melting points of the system in the following manner for concentrations of PCl_5 in excess of 30 mol.%: a mixture of PCl_5 and ICl of known composition was placed in a sealed test tube and kept in a thermostat until dissolution was complete and the liquid looked homogeneous to the naked eye; then the contents of the test tube were transferred to a thermal-analysis vessel, and the crystallization temperature was determined.

No determinations were made at high PCl_5 concentrations – in excess of, say, 50 mol.%, since the amount of PCl_6I that sublimed increased considerably. To prove that the sublimed substance actually was PCl_6I, we analyzed it, thus determining its composition.*

The results of the thermal analysis of the PCl_5–ICl system are listed in Table 4.

TABLE 4

Thermal Analysis of the PCl_5–ICl System

Mol. % PCl_5	Arrest points
ICl	27.1°
6.21	20.6
7.85	10.6
9.21	9.6
17.60	22.5
30.71	82.2
33.03	90.2
40.34	180.0

TABLE 5

Specific Conductance of Solutions of PCl_5–ICl

Mol. % PCl_5	Specific conductance of the system, $\kappa \cdot 10^2$	
	45°	55°
ICl	0.53	–
2.28	1.72	2.04
4.73	2.65	3.26
11.66	2.57	3.28
12.91	2.53	–
14.14	2.18	2.63

We measured the specific conductance of the PCl_5–ICl system at 45 and 55° at concentrations ranging up to 14 mol.% PCl_5. It was difficult to measure the conductance at high concentrations, since the minimum tone was very blurry under these conditions. The specific conductance measurements are listed in Table 5. They confirm our earlier observations [1,2] that PCl_6I (or $[PCl_4][ICl_2]$) is a rather strong electrolyte.

Conductance of PCl_6I and PBr_6I in some nonaqueous solutions. The PCl_6I and PBr_6I were prepared for these investigations as described in our previous reports.

We first made a rough determination of the solubility of these coordination compounds in the solvents listed below. We did this by adding weighed amounts of the coordination compound (in small batches at a time) to a definite amount of the solvent placed in a thermostat until no more dissolved, so that a slight amount of the solute remained in the solid phase. The conductance was measured at 20° in most cases. **

Whenever the coordination compounds were only sparingly soluble in the given

*The PCl_6I was analyzed chemically by the method described in an earlier report. [1].

**Whenever the temperature is not mentioned henceforth in stating the conductance values, it is 20°.

solvent – up to 0.5% by weight – the conductance values refer to the saturated solution. Whenever we were unable to determine the conductance in our apparatus, it was below 10^{-8} ohm^{-1} cm^{-1}.

PCl_3I solutions. PCl_3I is readily soluble in bromine and iodine chloride. The solutions display a rather high conductance of the order of 10^{-2} ohm^{-1} cm^{-1}. (Tables 6 and 7).

TABLE 6

Specific Conductance of PCl_3I Solutions in Bromine

Mol. % PCl_3I	$\varkappa$ at 25°
Bromine	Nonconductor
1.01	$4.55 \cdot 10^{-8}$
3.65	$7.03 \cdot 10^{-3}$
5.38	$1.02 \cdot 10^{-2}$
10.65	$2.00 \cdot 10^{-2}$
15.34	$2.00 \cdot 10^{-2}$
16.79	$1.89 \cdot 10^{-2}$ } Some grains of the substance remained undissolved

TABLE 7

Specific Conductance of PCl_3I Solutions in Iodine Chloride

Mol. % PCl_3I	$\varkappa \cdot 45°$	$\varkappa \cdot 55°$
2.31	$1.71 \cdot 10^{-2}$	$2.05 \cdot 10^{-2}$
4.88	$2.65 \cdot 10^{-2}$	$3.26 \cdot 10^{-2}$
13.03	$2.57 \cdot 10^{-2}$	$3.28 \cdot 10^{-2}$
16.31	$2.18 \cdot 10^{-2}$	$2.63 \cdot 10^{-2}$

PCl_3I is also readily soluble in molten iodine, forming highly conducting solutions, as we noted in our investigation of the PCl_5–I_2 system, in which PCl_3I is formed [1].

PCl_3I likewise dissolves in the following solvents (the figures in parentheses have the following significance: the first figure is the approximate solubility in % by weight; the second figure is the specific conductance in ohms^{-1} cm^{-1} at the given concentration): in acetonitrile (10.1%; $7.7 \cdot 10^{-3}$); in nitrobenzene (2.6%; $1.3 \cdot 10^{-3}$); in ethyl bromide (1.0%; $3.8 \cdot 10^{-5}$); and in chloroform (1.2%; $1.1 \cdot 10^{-5}$).

PCl_3I is only sparingly soluble (less than 0.5%) in the following solvents: carbon disulfide, benzene, toluene, xylene, carbon tetrachloride, bromobenzene, methyl iodide, ethyl iodide, and ethyl ether; the saturated solutions are nonconductors. Up to 1.5% PCl_3I is soluble in dioxane; the solution is a nonconductor.

PBr_3I solutions. Bromine and iodine bromide dissolve PBr_3I readily. The solutions have fairly high conductance – up to 10^{-2} ohm^{-1} cm^{-1} (Tables 8 and 9).

TABLE 8

Conductance of Solutions of PBr_3I in Bromine

Mol.% PBr_3I	$\varkappa \cdot 25°$
2.80	$5.49 \cdot 10^{-8}$
6.82	$1.59 \cdot 10^{-2}$
12.61	$2.38 \cdot 10^{-2}$
17.81	$1.99 \cdot 10^{-2}$

TABLE 9

Specific Conductance of Solutions of PBr_3I in Iodine Bromide

Mol. % PBr_3I	$\varkappa \cdot 45°$	$\varkappa \cdot 55°$
4.02	$2.51 \cdot 10^{-2}$	$2.84 \cdot 10^{-2}$
7.10	$3.40 \cdot 10^{-2}$	$3.81 \cdot 10^{-2}$
10.85	$3.41 \cdot 10^{-2}$	$3.81 \cdot 10^{-2}$
15.07	$3.01 \cdot 10^{-2}$	$3.62 \cdot 10^{-2}$
19.59	$2.47 \cdot 10^{-2}$	$2.91 \cdot 10^{-2}$
23.92	$1.98 \cdot 10^{-2}$	$2.40 \cdot 10^{-2}$
29.44	$1.48 \cdot 10^{-2}$	$1.88 \cdot 10^{-2}$

PBr_3I is readily soluble in molten iodine, forming highly conducting solutions, as ought to follow from the results of our investigation of the PBr_3–iodine system, in which PBr_3I is formed. The conductance of this system is $3.4 \cdot 10^{-2}$ ohm^{-1} cm^{-1} at 130° [2].

Solutions in acetonitrile (13.0%, $3.4 \cdot 10^{-3}$ ohm^{-1} cm^{-1}), in nitrobenzene (9.3%, $1.1 \cdot 10^{-3}$), ethyl bromide (7.0%, $1.1 \cdot 10^{-3}$), and chloroform (8.0%, $3 \cdot 10^{-5}$), are also

conductors. Carbon disulfide, benzene, toluene, carbon tetrachloride, bromobenzene, and dioxane dissolve small amounts of PBr_3I, but these solutions are nonconductors.

A comparison of the behavior of PCl_3I and PBr_3I in various solvents indicates that the latter coordination compound is, in general, more highly soluble in various solvents than PCl_3I. This is seen in the solubility of these coordination compounds in chloroform, ethyl bromide, and nitrobenzene.

Both of these coordination compounds have approximately the same conductance in solutions. Solutions in bromine, iodine, and iodine chloride or bromide exhibit the highest conductance, followed by solutions in ethyl bromide.

Cryoscopic investigations. The PCl_5–ICl–$C_6H_5NO_2$ System. The Beckman method was used in our cryoscopic investigations.

The results of these investigations are listed in Table 10 and plotted in Fig. 3. In the table, $t°$ is the freezing point in the Beckmann thermometer;

TABLE 10

Cryoscopic Investigation of the PCl_5–ICl System in Nitrobenzene

Grams of $C_6H_5NO_2$	Grams of ICl	Grams of PCl_5	Mol.% PCl_5 (in terms of ICl + PCl_5)	Freezing point, t°	Δt_0	Δt
22.217	–	–	–	4.525°	–	–
22.217	0.1178	–	–	4.301	0.224	–
22.217	0.1178	0.0889	36.83	4.178	–	0.123
22.217	0.1178	0.1188	44.18	4.138	–	0.166
22.217	0.1178	0.1583	51.35	4.110	–	0.191
22.217	0.1178	0.1773	54.15	4.053	–	0.248
22.217	0.1178	0.2344	60.87	3.963	–	0.338
22.217	0.1178	0.3002	66.66	3.952	–	0.349

TABLE 11

Cryoscopy of a Solution of PCl_3I* in Nitrobenzene

Grams of $C_6H_5NO_2$	Grams of PCl_3I	Wt.% PCl_3I	Δt	Molecular weight
23.646	0.0617	0.26	0.095	180.3
23.646	0.2327	0.97	0.370	183.2
23.646	0.3569	1.47	0.550	189.1

Δt_0° is the depression of the freezing point caused by iodine chloride; $\Delta t°$ is the change in the depression observed when PCl_5 is added to the solution of ICl in nitrobenzene.

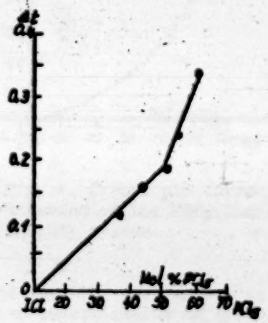

Fig. 3. Cryoscopic investigation of the PCl_5–ICl–$C_6H_5NO_2$ system.

As we see from the data, adding PCl_5 to ICl in nitrobenzene solution increases the depression, but after the equimolar proportions of PCl_5 and ICl have been reached, corresponding to the composition of the coordination compound PCl_3I, the depression of the solution increases still more, owing to the appearance of excess PCl_5 molecules in the solution, which do not go to make up the coordination compound.

* The molecular weight of PBr_3I from the formula is 637.5

To learn the state of the PCl_5I coordination compound in the solution, we made cryoscopic investigations, the results of which are listed in Table 11.

We found that the molecular weight of PCl_5I was nearly halved in a nitrobenzene solution, which may be caused by the electrolytic dissociation of this coordination compound into two ions, $PCl_5I = [PCl_4][ICl_2]$ [1], as well as by its possible partial decomposition into its initial constituents PCl_5 and ICl.

The PBr_5–IBr–$C_6H_5NO_2$ System. The results of our cryoscopic investigations of the PBr_5–IBr system and of the PBr_5I coordination compound are listed in Tables 12 and 13 and plotted in Fig. 4. The nature of the changes in the depression

TABLE 12

Cryoscopic Investigation of the PBr_5–IBr System in Nitrobenzene

Grams of $C_6H_5NO_2$	Grams of IBr	Grams of PBr_5	Mol.% PBr_5 (in terms of IBr + PBr_5	Freezing point, t°	Δt_0°	Δt°
26.309	–	–	–	4.468	–	–
26.309	0.1678	–	–	4.242	0.226	–
26.309	0.1678	0.1605	31.36	4.080	–	0.162
26.309	0.1678	0.2387	44.52	3.960	–	0.282
26.309	0.1678	0.3402	49.05	3.901	–	0.341
26.309	0.1678	0.3834	52.07	3.812	–	0.430
26.309	0.1678	0.5603	61.65	3.600	–	0.642

TABLE 13

Cryoscopy of a Solution of PBr_5I** in Nitrobenzene

Grams of $C_6H_5NO_2$	Grams of PBr_5I	Wt. % PBr_5I	Δt	Molecular wt. of PBr_5I
25.447	0.1218	0.44	0.092	358.6
25.447	0.1961	0.78	0.150	353.9

with changes in the PBr_5:IBr ratio (Table 12 and Fig. 4), like those observed for the PCl_5–ICl system in nitrobenzene, indicate that PBr_5 and IBr form a coordination compound with the composition of PBr_5–IBr in nitrobenzene.

The lowered molecular weight of PBr_5I (almost by half) is due to the same causes*** as were observed in determining the molecular weight of PCl_5I.

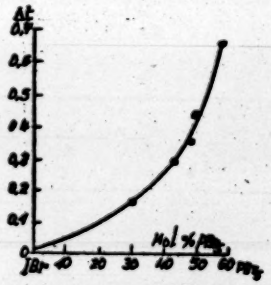

Fig. 4. Cryoscopic investigation of the PBr_5–IBr–$C_6H_5NO_2$ system.

The results of our investigation of the PCl_5–ICl and PBr_5–IBr systems are in good agreement with the results we obtained in our earlier investigation of systems with the composition of PX_5–I_2 and PX_5–IX (X = Cl or Br, respectively). As stated above, in the latter two groups of systems the coordination compounds PCl_5 – ICl and PBr_5–IBr are formed, as follows: when PCl_5 (or PBr_5) reacts with iodine, we first get ICl (or IBr), which then combines with the unreacted PCl_5 or PBr_5, to for a coordination compound of the above composition. Similarly, in the PX_5–IX systems, first PX_5 is formed, then combining with IX to yield the coordination compound PX_5I.

Our investigations of the PCl_5–ICl and PBr_5–IBr systems has fully confirmed

The specific conducatance of the solutions we tested was of the order of 10^{-4} ohm^{-1} cm^{-1}.

**See footnote Table 11. ***The specific conducatance of dilute solutions of PBr_5I in nitrobenzene is of the order of 10^{-4} ohm^{-1} cm^{-1}.

this concept, proving the identity of the coordination compounds formed in all these three groups of systems. The results of this research, which also bear out that the coordination compounds PCl_6I and PBr_6I possess the properties of fairly strong electrolytes, are in agreement with the concept of these coordination compounds set forth in our previous reports as double halides (containing a phosphonium cation tetrasubstituted by a halogen), the formation of which when PCl_5 (or PBr_5) is reacted with ICl (or IBr) may be represented by means of the following equation:

$$[PX_4]X + IX = [PX_4][IX_2].$$

SUMMARY

1. The fusibility curves of the PBr_5–IBr and PCl_5–ICl systems have been plotted. The results obtained support the conclusion that coordination compounds with the equimolar composition of $PCl_5 \cdot ICl$ and $PBr_5 \cdot IBr$ are formed in these systems.

2. The PCl_5–ICl and PBr_5–IBr systems possess fairly high conductance – of the order of 10^{-2} ohm^{-1} cm^{-1} – due to the electrolytic dissociation of the PX_6I coordination compounds.

3. Cryoscopic investigations of the PCl_5–ICl and PBr_5–IBr systems in nitrobenzene solutions has indicated that coordination compounds of the foregoing composition are also formed in these solutions as well.

The molecular weight of these coordination compounds is nearly halved in nitrobenzene, compared to the theoretical values, which may be attributed to the electrolytic dissociation of the PCl_6I and PBr_6I (or $[PX_4][IX_2]$) and to the partial decomposition of the latter in nitrobenzene solutions.

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* See CB translation p. 797 ff.

** See CB translation p. 997 ff.

*** See CB translation p. 479 ff.

A SPOT REACTION FOR COBALT, USING DIMETHYLAMINOANTIPYRINE

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As the researches of S.I.Gusev [1] and D.I.Ryabchikov [2] have shown, several pyrazolone derivatives, especially dimethylaminoantipyrine (pyramidon), $C_{13}H_{17}ON_3$, form difficultly soluble coordination compounds with such elements as Zn, Co, Cu, the rare earths, and others. Introducing pyramidon makes the molecules of coordination compounds considerably heavier, which usually lowers the solubility of the coordination compounds, on the one hand, and increases the stability of the coordination compounds thenselves, on the other.

Thus, though the coordination compound $(NH_4)_2[Co(CNS)_4]$ is relatively unstable, high concentrations of the reagents, or the use of a specific solvent for this coordination compound being required to produce a blue color (the well-known Vogel [3] reaction for cobalt), adding pyramidon to the solution results in the formation of a rather sparingly soluble, stable coordination compound, the composition of which is $(Pyr)_2H_2[Co(CNS)_4]$,* according to S.I.Gusev, who was the first to prepare and describe this coordination compound.

The state of affairs is similar for other elements. Zinc, for example, reacts with pyramidon and thiocyanogen ions in an acid medium to form the rather sparingly soluble compound $(Pyr)_2H_2[Zn(CNS)_4]$.

Closer study of the formation of coordination compounds of cobalt, pyramidon, and thiocyanogen ions has shown that the composition of the compounds depends upon the medium in which the formation of the coordination compound takes place.

While S.I.Gusev carried out the reaction in acid media and secured the coordination compound $(Pyr)_2H_2[Co(CNS)_4]$ mentioned above, which consisted of lustrous light-blue (cornflower-blue) crystals, we secured a compound of different composition and properties in media that were more nearly neutral. The coordination compound secured under such conditions consists of lustrous lilac-colored crystals, with the composition of $Co(Pyr)_2(CNS)_2$. Its solubility was barely one-fourth of that of the coordination compound synthesized by S.I.Gusev, amounting to 0.019 g per 100 ml of water (in terms of cobalt). If we vary the acidity of the medium, we can observe the reciprocal transformation of these coordination compounds, the typical picture of a reversible process, which can be represented by the following equation:

$$(Pyr)_2H_2[Co(CNS)_4] \rightleftharpoons Co(Pyr)_2(CNS)_2 + 2H^+ + 2CNS^-.$$

The coordination compound $[Co(Pyr)_2(CNS)_2]$ (lilac-colored) exists at a pH in excess of 5-6. It is converted into the blue $(Pyr)_2H_2[Co(CNS)_4]$ by increasing the acidity of the medium.

Our attention was attracted to the possibility of utilizing these colored coordination compounds for the qualitative detection of cobalt. An attempt to make a direct qualitative determination of cobalt by utilizing its formation

*Pyr - an abbreviation for pyramidon, which we shall use henceforth.

of a coordination compound with pyramidon and thiocyanogen ions in an acid medium yielded no results, owing to the ease with which supersaturated solutions were formed. When the quantity of cobalt present was small, it sometimes took hours for the precipitate to form.

Thus the only way to solve the problem of detecting cobalt by the use of pyramidon was to find a way of eliminating the supersaturation phenomena quickly. We therefore made a study of the processes involved in the formation of coordinations compounds of pyramidon and other elements, particularly with zinc. When zinc forms a coordination compound with pyramidon and thiocyanogen ions, the phenomenon of supersaturation, though present, is on a much smaller scale than in the case of cobalt.

We observed the following rather interesting phenomenon: When solutions of zinc and cobalt, which did not yield precipitates by themselves when a solution of pyramidon and ammonium thiocyanate was added, were mixed together, a small, but clearly apparent, blue precipitate was immediately thrown down. A more detailed investigation of the processes involved in the formation of coordination compounds of zinc and cobalt with pyramidon showed that the coordination compounds of zinc and cobalt formed in acid media were isomorphic.

Both coordination compounds crystallize in the monoclinic system, prismatic type. The crystals are a combination of the following simple forms: a prism of the third order (110); a second pinacoid (010); a third pinacoid (001); and, probably, a prism of the first order (011). The habit of the crystal is prismatic; the crystals are acicular, elongated in the direction of the principal prism.

The isomorphism is proved by the following structural data of the crystals.

1. The (blue) crystals of the cobalt coordination compound grow on (are added on to) the (colorless) zinc coordination compound so that the addition process terminates in the formation of a more or less complete monocrystal, consisting of both constituents, this being expressed in the formation of faces of a third pinacoid (001).

This is expecially characteristic of the crystal fragments, which endeavor to form complete crystals in a saturated solution of the zinc coordination compound.

2. The cleavage fissures, which are parallel to the faces of the principal prism in the cobalt coordination compound continue in the zinc coordination compound when the latter is added on to the former.

We utilized the isomorphism of these zinc and cobalt coordination compounds and the absence of supersaturation when both cations are present in the solution in developing a qualitative reaction for cobalt.

When a small amount of zinc is added to a solution that contains cobalt, followed by the addition of a solution of pyramidon and ammonium thiocyanate, a blue or light blue precipitate (depending on the amount of cobalt present) is thrown down at once. It is best to perform this as a spot reaction. The spot method ensures greater sensitivity of the reaction and represents a saving in reagents.

The reaction is carried out as follows: a drop of the reagent, consisting of a pyramidon and ammonium thiocyanate dissolved in dilute hydrochloric acid, is placed on a filter paper, followed by a drop of the zinc solution and another drop of the reagent. Fifty to sixty seconds later (the time required for the complete formation of the zinc coordination compounds) a drop of the unknown solution is applied, followed by another drop of the reagent. If cobalt is present, a characteristic light-blue spot will appear.

The sensitivity of the reaction is enhanced appreciably by the fact that the cobalt coordination compound is formed as a thin layer upon the already formed crystals of the zinc coordination compound, which spreads over the surface of these crystals, and grows on them, so that the light-blue color is readily visible even when the amount of cobalt is very small. This reaction makes it possible to detect as little as 0.4 microgram of cobalt without difficulty or subsequent manipulations.

The sparing solubility of the coordination compound, its high molecular weight, and the utilization of the isomorphism phenomenon combine to provide an appreciable increase in the sensitivity of the reaction over the well-known Vogel reaction [4] for cobalt.

We also explored the feasibility of using the coordination compound $Co(Pyr)_2(CNS)_2$ in a qualitative test for cobalt, but inasmuch as the presence of many cations of the ammonium sulfide group interferes with this reaction in media that are nearly neutral, its use is less advisable.

EXPERIMENTAL

As stated above, the cobalt reagent is a solution of pyramidon and ammonium thiocyanate in dilute hydrochloric acid. We prepared several solutions, containing various proportions of pyramidon, ammonium thiocyanate, and hydrochloric acid to select the most suitable concentrations of these constituents. A solution containing 4.0 g of ammonium thiocyanate, 1.6 g of pyramidon, and 16 ml of 2N hydrochloric acid per 100 ml of solution was found to be best, from the standpoint of stability and sensitivity of the cobalt reaction.

The other solution used in carrying out this reaction is a 2% solution of zinc sulfate ($ZnSO_4 \cdot 7H_2O$).

We investigated the concentration limit at which cobalt can be detected, as well as the detectable minimum. The acidity of the test solutions varied from 0.5 to 1.0 N of hydrochloric acid, i.e., we used a fairly wide range of acidities, corresponding to what is generally employed for qualitative determinations.

After carrying out the reaction with pure salts, we investigated the feasibility of detecting cobalt in the presence of other cations. Our results are listed in the subjoined table.

As the table indicates, the detection limit of cobalt is 0.4 γ, for a drop size of 0.003-0.004 ml at a concentration limit of 1:10000.

Cations of the alkali and alkali-earth elements do not interfere with the test. Nor do cations of the ammonium sulfide group, with the exception of trivalent iron, affect the determination of cobalt in mineral acid media throughout a wide range of concentrations.

Ions such as chromium and nickel impart their characteristic color to the paper at high concentrations, but these cations move out to the periphery of the spot when the reagent is added and do not interfere with the detection of the cobalt.

Trivalent iron, which produces a bright color with ammonium thiocyanate, interferes with the test and should be reduced beforehand. When this spot test is employed during the course of a systematic analysis, the difficulties introduced by iron do not arise, since the iron is reduced during the analysis, the cobalt being detectable directly after the elimination of the second group of cations and the hydrogen sulfide.

The method involving the masking of the iron by fluoride salts cannot be employed with the high concentrations of thiocyanate ions required in the reagent.

Results of the Qualitative Determination of Cobalt in the Presence of other Elements (Concentration Limit = 1:100000)

Test No.	Acidity of the HCl solution (normality of the acid	Foreign substances present and their concentration (in per cent)		Detection limit, micrograms
1	0.05	$NiCl_2 \cdot 6H_2O$	10	0.4
2	1.0			0.4
3	0.05	$Cr_2(SO_4)_3 \cdot 18H_2O$	10	0.3
4	1.0			0.4
5	0.05	$MnCl_2 \cdot 4H_2O$	15	0.3
6	1.0			0.4
7	0.05	$Al_2(SO_4)_3 \cdot 18H_2O$	20	0.3
8	1.0			0.4
9	0.05	NaCl	10	0.3
10	1.0			0.3
11	0.05	KCl	10	0.3
12	0.05	$BaCl_2 \cdot 2H_2O$	10	0.3
13	1.0			0.3
14	0.05	$CaCl_2 \cdot 6H_2O$	10	0.3
15	1.0			0.3
16	1.0	NH_4Cl	10	0.3
17	0.05	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	10	0.6
18	1.0			0.6

The reaction medium must be clearly acid, since different coordination compounds are formed in neutral or nearly neutral media, as has been pointed out, which include other elements of the ammonium sulfide group.

SUMMARY

1. It has been shown that, in addition to the coordination compound $(Pyr)_2H_2[Co(CNS)_4]$, produced by S.I.Gusev in acid media, cobalt may form another coordination compound, $Co(Pyr)_2(CNS)_2$.

2. These coordination compounds can be converted into each other by varying the acidity of the medium.

Though only the coordination compound $(Pyr)_2H_2[Co(CNS)_4]$ exists at a pH of the medium below 3-4, this compound is entirely converted to the coordination compound $Co(Pyr)_2(CNS)_2$ when the pH is in excess of 6.

3. The coordination compounds of zinc and cobalt, $(Pyr)_2H_2[Zn(CNS)_4]$ and $(Pyr)_2H_2[Co(CNS)_4]$, have been found to be isomorphous, and this isomorphism has been utilized to heighten the sensitivity of the cobalt reactions.

4. A new method for the qualitative determination of cobalt by a spot test is suggested, involving the use of pyramidon.

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THE REACTION OF METALLIC IRON WITH ETHYL BROMIDE

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The problem of the existence of organometallic compounds of iron is of considerable importance in chemistry as well as in biology, in view of the important and as yet unknown role that iron plays in the process of photosynthesis. All efforts to prepare such compounds have been uniformly unsuccessful, however. Neither Wanklyn and Carius [1], who reacted ferrous iodide with diethylzinc, nor Kondyrev and Fomin [2], who reacted ethylmagnesium bromide with iron halides, met with success. Later, Job and Reich [3,4] reacted ferrous iodide with diethylzinc and believed they had prepared the mixed organoiron compound C_2H_5FeI, since water precipitated green $Zn(OH)_2$ from the reaction product, rather than the white $Fe(OH)_2$; the authors were unable, however, to isolate this supposed compound. Nor was Lichtenwalter [5] able to secure organoiron compounds by reacting iron halides with tetraethyllead.

In view of the analogies between iron and aluminum we thought it might be possible to produce organoiron compounds by reacting metallic iron directly with ethyl bromide, since similar treatment of aluminum readily yields organoaluminum compounds, as was proved long ago by Grignard [6,7], and subsequently confirmed by Grosse and Mavity [8].

We proceeded as follows: a small quantity (0.1-0.2 g) of finely powdered pure iron (Standard Sample No. 126 of the Urals Institute of Metals, labeled as containing 99.54% iron) was pickled in hydrochloric acid and then carefully washed with water, alcohol, and ether and dried. It was then placed in a small Erlenmeyer flask and treated with a considerable excess (3-5 g) of absolute, anhydrous, freshly distilled ethyl bromide (b.p. 38°). When the flask contents were agitated, the ethyl bromide immediately turned yellow, changing to orange after standing for 10-15 minutes. Further standing produced no change in the intensity of the color. The colored ethyl bromide was decanted from the unreacted iron into a small Würtz flask and driven off over a water bath. A greasy, dark red, nearly black substance was left in the flask, which solidified into orange red crystals after being kept for 48 hours in a vacuum desiccator. The yield is small – of the order of 0.1-0.2 g. The substance is readily soluble in ether and benzene, coloring them a bright red. Water decolorizes these solutions at once, the aqueous solution exhibiting the qualitative reactions for trivalent iron and bromine. When heated, the substances fuses with decomposition, liberating a gas with a burnt odor and leaving behind a blackish-brown powder that is partially soluble in hydrochloric acid. The hydrochloric acid solution exhibits the reaction for trivalent iron. The residue that is insoluble in hydrochloric acid is a light black powder, which proved to be carbon upon analysis.

0.1236 g substance: 0.0738 g CO_2; 0.0396 g H_2O. 0.1644 g substance: 0.0972 g CO_2; 0.0520 g H_2O. Found %: C 16.29, 16.12; H 3.56, 3.52. $(C_2H_5)_2FeBr + (C_2H_5)FeBr_2$. Computed %: C 16.41; H 3.45.

Amyl bromide and bromobenzene yield similar reactions with iron.

SUMMARY

A reaction of metallic iron with ethyl bromide had been discovered, which results in the formation of an equimolar mixture of diethylferric bromide and ethylferric dibromide, in accordance with the equation:

$$2Fe + 3C_2H_5Br = (C_2H_5)_2FeBr + (C_2H_5)FeBr_2,$$

which proves, for the first time, that organoiron compounds do exist.

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COORDINATION COMPOUNDS CONTAINING ANIONS OF AROMATIC SULFO ACIDS IN THEIR OUTER SPHERE

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In an earlier report [1] we discussed the general behavior patterns involved in the solubility of complex salts; we demonstrated that the least soluble salts are formed when complex ions combine with ions of opposite charge that possess the following characteristics: 1) rather large dimensions, so as to provide the optimum ionic radii ratio; 2) as high a charge as possible; 3) the ions must contain no hydrophilic groups, i.e., groups that can enter into a chemical bond with water molecules (OH, RCOO, NH_2, etc.); and 4) the polar groups in the ions must result in a diminution of the solubility of the salt. In the light of these considerations, anions of aromatic sulfo acids ought to form rather sparingly soluble salts with complex cations, provided these anions do not contain the groups OH, NH_2, etc., and it may be assumed that the presence of the groups NO, Cl, Br, I, and NR_2 in the sulfonate ions ought to result in a decrease in the solubility of the corresponding salts.

Ephraim's qualitative experiments [2] have established that some anions of aromatic sulfo acids actually do form sparingly soluble salts with complex cations; Ephraim did not investigate the conditions under which these sparingly soluble precipitates are formed nor their composition, however. Moreover, the number of sulfo acids investigated by Ephraim was not very high, and the author made no effort to provide a theoretical explanation for the observed behavior patterns. And yet, an investigation of these compounds is of obvious interest from the practical as well as the theoretical point of view, since finding the conditions required for securing sparingly soluble salts of cations of the sulfo acids would make it possible to separate the respective sulfo acids from their solutions by utilizing complex cations. (This property has already been exploited by A.N. Kurakin [3] at our suggestion). On the other hand, sulfo acid anions could be utilized to recover various compounds of rather unstable complex cations from solutions.

In the light of the foregoing, we undertook an investigation of complex salts having sulfo acid anions in their outer sphere. Large triply charged ions: $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, and $[Cr(CON_2H_4)_6]^{3+}$, were chosen as the complex cations. These cations were combined with anions of various aromatic sulfo acids that had not been investigated by Ephraim [2].

EXPERIMENTAL

We used saturated solutions of the complex salts $[Co(NH_3)_6]Cl_3$, $[Cr(NH_3)_6](NO_3)_3$, $[Cr(CON_2H_4)_6]Cl_3$, and approximately 1% solutions of the sodium salts of the sulfo acids in question to prepare the salts to be tested. In the overwhelming majority of cases a precipitate of the respective sulfonate was formed when the test solutions were poured together.

We then investigated the concentration limits of the solutions of the sodium

salts of the sulfo acids at which the formation of a precipitate could still be detected in 1 ml of solution.

In some instances the resulting precipitates were suction-filtered, desiccated, and subjected to chemical analysis for one of their components. In others, the solubility was determined by the "synthetic method." [4].

Salts of dimethylaminobenzenesulfonic acids. A solution of sodium p-dimethylaminobenzene sulfonate yields a crystalline precipitate when treated with solutions of $[Co(NH_3)_6]Cl_3$ and $[Cr(CON_2H_4)_6]Cl_3$, the precipitate with the luteo salt being formed at a concentration limit of 1:100, while the concentration limit for the solution of the hexaureachromic salt is 1:140. The compound $[Co(NH_3)_6](C_8NH_{10}SO_3)_3$ formed in these reactions was investigated more closely. It was found to contain 7.79% of cobalt, the calculated value being 7.73%. The solubility of this salt is 0.0037 mol per liter at 20°.

It should be noted that the m-dimethylaminobenzene sulfonate forms a precipitate only when highly concentrated solutions of both components are mixed together, whereas the salts of sulfanilic acid do not form precipitates at all under the conditions described.

Salts of substituted toluenesulfonic acids. Sodium 2-chlorotoluene sulfonate-4 forms crystalline precipitates with all three solutions of the complex salts. The concentration limits are about the same for all three solutions, being 1:200 for the chromium luteonitrate and hexaureachromichloride and 1:250 for the cobaltic luteochloride. 2-Chlorotoluene sulfonates-4 with two complex cations were isolated and analyzed. $[Co(NH_3)_6](C_7H_6ClSO_3)_3$ consists of yellow crystals; it contains 7.02% cobalt; the computed figure is 6.96%. $[Cr(CON_2H_4)_6](C_7H_6ClSO_3)_3$ consists of green prismatic crystals; it contains 5.01% chromium; the computed figure is 5.05%.

Sodium 2-nitrotoluene sulfonate-4 likewise forms crystalline precipitates with all the complex salt solutions tested; here the concentration limits are somewhat higher, however. Thus, for example, the concentration limit is 1:100 for the solution of $[Cr(NH_3)_6](NO_3)_3$. All three resulting salts were recovered from solution and analyzed. $[Co(NH_3)_6](C_7H_6NSO_5)_3$ – yellow crystals – contained 7.10% cobalt; the computed figure was 7.20%. $[Cr(NH_3)_6](C_7H_6NSO_5)_3$ – yellow crystals – contained 6.53% chromium; the calculated figure was 6.48%. The solubility at 40° was 0.0087 mol per liter. $[Cr(CON_2H_4)_6](C_7H_6NSO_5)_3$ – green acicular crystals – contained 4.92%; the calculated figure was 4.91%. The solubility of this salt at 20° was 0.0033 mol per liter.

Lastly, sodium 2-chloro-5-nitrotoluene sulfonate-4 likewise forms crystalline precipitates with all three of the tested complex salts; here, however, the concentration limits are still higher than for nitrotoluenesulfonic acid. They are 1:80 for the chromium and cobalt luteo salts and 1:180 for the hexaureachromichloride. The fact that the isomeric 2-chloro-2-nitrotoluene sulfonate-4 can be precipitated from a solution of the hexaureachromichloride only at a concentration of 1:50 is worthy of note. Two of the salts we secured were analyzed. $[Cr(NH_3)_6](C_7H_5ClNSO_5)_3$ – yellow crystals – contained 5.02% chromium; the computed figure was 5.04%. $[Cr(CON_2H_4)_6](C_7H_5ClNSO_5)_3$ – prismatic green crystals – contained 4.45 and 4.50% chromium; the calculated figure was 4.47%.

Salts of carbazolsulfonic acids. Sodium 3-carbazol sulfonate forms precipitates with the complex salts in question even in quite dilute solutions. The concentration limits for the test solutions were as follows: 1:1700 for the $[Co(NH_3)_6]Cl_3$ solution and 1:500 for the $[Cr(CON_2H_4)_6]Cl_3$ solution. In every case amorphous precipitates were formed whose colors were those of the respective complex salts.

The salts of 6-nitrocarbazolsulfonic-3 acid proved to be even more sparingly

In every case the concentration limits are stated for the sulfonates.

soluble. The concentration limits were 1:3300 for the cobaltic luteochloride and 1:5000 for the hexaureachromichloride. The reaction products were isolated and analyzed. $[Co(NH_3)_6](C_{12}H_6N_2SO_5)_3$ – a yellow amorphous substance – contained 5.64% cobalt; the calculated figure was 5.70%. $[Cr(CON_2H_4)_6](C_{12}H_6N_2SO_5)_3$ – a yellow amorphous substance – contained 4.02 and 4.07% chromium; the calculated figure was 4.04%.

It should be noted that the nitrocarbazol sulfonates form precipitates not merely with the rather stable triply charged complex ions, but with the relatively unstable ammoniacal cations of copper, zinc, nickel, and cadmium as well.

Salts of alizarinsulfonic acid. The alizarin sulfonates of the complex ions we have been discussing display even lower solubility. In these cases the concentration limits are 1:33,000 for the cobaltic luteochloride and 1:20,000 for the hexaureachromichloride. Chemical analysis of the hexamminechromializarin sulfonate yielded the following result: chromium content 5.40%; calculated figure 5.06%. The reasons for the increased percentage of chromium in this precipitate remained unknown (the calculation was based on $[Cr(NH_3)_6](C_{14}H_7O_4SO_3)_3$).

Evaluation of Results

Several interesting conclusions can be drawn from our experimental data, which bear out to a certain extent the theoretical presuppositions that underlay the investigation.

The first thing we notice is the analogy in the behavior of all three of the complex ions investigated: $[Cr(NH_3)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, and $[Cr(CON_2H_4)_6]^{3+}$, despite the fact that they differ in the nature of the central atom as well as in the nature of the coordinated groups. The analogy in the solubility of the respective salts may be traced for all the cases of salts with these cations described in the literature. Apparently, this similarity is due to the fact that all these ions have three charges and have approximately the same dimensions (at least in the first two cases).

The solubility of these salts with anions of the sulfo acids in the outer sphere diminishes as the size of the anion increases. None of the complex ions investigated forms a precipitate with a benzene sulfonate ion under the conditions studied; precipitates are formed with the toluene sulfonate ion only in highly concentrated solutions; while the carbazol sulfonate ion precipitates the ions under investigation even at high dilutions. The literature contains references to the sparing solubility of complex β-naphthalene sulfonates. The large dimensions of the alizarin sulfonate ion causes it to form sparingly soluble salts with the complex cations, notwithstanding the fact that it contains two hydroxyl groups.

The presence of polar groups (NO_2, Cl, NR_2) in the sulfonate ions results in a decrease in the solubility of the respective salts formed with the complex cations, all other conditions remaining the same. The presence of groups that can enter into a chemical bond with molecules of water (OH, NH_2, the carboxyl group) in the sulfonates sharply increases the solubility of the complex salts.

We tested a series of amino sulfo acids and hydroxy sulfo acids of the naphthalene series; in none of these instances, however, were we able to discover any precipitate when solutions of these sulfo acids were mixed together with solutions of the tested complex salts.

In some instances the complex salts can be utilized to separate isomeric sulfo acids (para and meta dimethylaminosulfo acids, chloronitrotoluenesulfo acids). We have been unable to derive any relationships governing the variation of the salt's solubility with the arrangement of the substituents in the sulfonate ion,

owing to the limited amount of material at our disposal.

Lastly, our experiments support the conclusion that large anions of sulfo-acids, especially those containing the substituents mentioned above, can be utilized to precipitate rather diversified complex cations.

SUMMARY

1. It has been established that the complex cations $[Co(NH_3)_6]^{3+}$, $[Cr(NH_3)_6]^{3+}$, and $[Cr(CON_2H_4)_6]^{3+}$ form sparingly soluble salts with the anions of several aromatic sulfo acids. The solubility of the resulting salts decreases in approximately the following order: 2-chloro-5-nitrotoluene sulfonate-4, 2-nitrotoluene sulfonate-4, p-dimethylamino sulfonate, 2-chlorotoluene sulfonate-4, 3-carbazol sulfonate, 3,6-nitrocarbazol sulfonate, and alizarin sulfonate.

2. The following 11 salts have been synthesized and their composition determined: a) hexammine cobaltic salts: of p-dimethylaminobenzenesulfonic acid; of 2-chlorotoluenesulfonic-4 acid; of 2-nitrotoluenesulfonic-4 acid; and of 3,6-nitrocarbazolsulfonic acid; b) hexammine chromic salts: of 2-nitrotoluenesulfonic-4 acid; of 2-chloro-5-nitrotoluenesulfonic-4 acid; and of alizarinsulfonic acid; c) hexaurea chromic salts: of 2-chlorotoluenesulfonic-4 acid; of 2-nitrotoluenesulfonic-4 acid; of 2-chloro-5-nitrotoluenesulfonic-4 acid; and of 3,6-nitrotoluenesulfonic acid.

3. The general behavior patterns governing the solubility of the tested complex salts with sulfo acid anions in their outer spheres have been established, viz.: the solubility decreases as the dimensions of the anion increase and when polar groups are introduced into it. The solubility of the test salts rise sharply when OH, NH_2, and carboxyl groups are introduced into the sulfo acid anion. It has been shown that coordination compounds may be employed to separate isomeric sulfo acids.

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SALTS OF ALKYL CARBONIC ACIDS (ALKYL CARBONATES OF THE METALS). I

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The objective of the present investigation is a study of the alkyl carbonates ROCOOMe.

Although the simplest alkyl carbonates have been known for a long time, we have no detailed and systematized data on them; nor have we their physicochemical constants or data on their thermal decomposition or the mechanism underlying the latter. We have been unable to find any data at all in the literature on many of the alkyl carbonates we have prepared and investigated.

Dumas and Peligot [1] were the first to prepare barium methyl carbonate, $(CH_3OCOO)_2Ba$, by passing anhydrous carbon dioxide through anhydrous baryta dissolved in absolute methyl alcohol. Destrem [2] synthesized barium ethyl carbonate, $(C_2H_5OCOO)_2Ba$, by passing carbon dioxide through barium ethoxide. Dumas and Peligot prepared (and partially investigated) potassium ethyl carbonate, C_2H_5OCOOK, by passing anhydrous carbon dioxide through caustic potash dissolved in absolute alcohol. Habermann [3] synthesized a similar salt by electrolyzing potassium acetate dissolved in ethyl alcohol, while Holmberg [4] synthesized it by reacting carbon dioxide with potassium hydrosulfide dissolved in absolute alcohol and with potassium ethyl mercaptide. F.Beilstein [5], expecting to synthesize lactic acid and with this in mind investigating the reaction of carbon dioxide upon sodium ethoxide, synthesized sodium ethyl carbonate, $C_2H_5OCOONa$, isomeric with sodium lactate. Geuther [6] prepared it by reacting sodium ethoxide with ethyl carbonate. Szarvasy [7] synthesized magnesium methyl carbonate, $(CH_3OCOO)_2Mg$, by reacting carbon dioxide with magnesium methoxide, while Szilard [8] produced magnesium ethyl carbonate, $(C_2H_5OCOO)_2Mg$, by electrolyzing a 1% solution of sodium ethoxide as an electrolyte, using a magnesium anode. V.E.Tishchenko [9] prepared aluminum ethyl carbonate, i.e., a "basic" salt of ethyl carbonic acid, as it were, by reacting carbon dioxide with aluminum ethoxide wetted down with anhydrous benzene. In the aromatic series, the reaction of carbon dioxide with the phenoxides is the basis for the Kolbe [10] synthesis of salicylic acid. Sodium phenyl carbonate can be prepared by saturating the phenoxide with carbon dioxide at ordinary temperature, as stated by R. Schmitt [11].

EXPERIMENTAL

Sodium ethyl carbonate, $C_2H_5OCOONa$, was prepared by passing carbon dioxide through sodium ethoxide. The resulting product was filtered out, washed with absolute ether, desiccated in a current of hydrogen, and then analyzed to determine its sodium content. The latter was determined by converting the sodium ethyl carbonate into sodium sulfate.

0.4578 g substance: 0.2893 g Na_2SO_4. 0.4980 g substance: 0.3168 g Na_2SO_4. Found %: Na 20.46, 20.60. $C_2H_5OCOONa$. Computed %: Na 20.54.

Sodium ethyl carbonate is a white crystalline substance that is very slightly

soluble in ether, ethyl alcohol, chloroform, acetone, and carbon disulfide. It is somewhat more soluble in methanol; the solubility rises as the temperature is raised. The salt dissolves in water with an alkaline reaction, it being hydrolyzed to sodium bicarbonate and ethyl alcohol. Like other alkyl carbonates, sodium ethyl carbonate may be employed to titrate acids.

Thermal decomposition. There are only a few statements concerning the dry distillation of barium methyl carbonate in Dumas and Peligot, who simply found that a combustible gas and a negligible quantity of an ethereal liquid were formed. As for the potassium ethyl carbonate, they noted the presence of potassium carbonate mixed with carbon in the residue, in addition to their comment on the evolution of gas. These authors evidently thought that the combustible gas was ethylene. Ritchy [12] investigated the thermal decomposition of complete carbonic acid esters. C. Faurholt [13] investigated the vapor tension of carbon dioxide above sodium ethyl carbonate and pointed out that heating results in the evolution of a gas, which was not even carbon dioxide, but ethylene.

The experiments we conducted on the thermal decomposition of the sodium ethyl carbonate actually yielded the stated products (ethylene, carbon dioxide, alcohol, and water).

$$C_2H_5OCOONa \rightarrow C_2H_4 + NaHCO_3.$$

Decomposition of $NaHCO_3$ yields soda, carbon dioxide, and water; the latter hydrolyzes the sodium ethyl carbonate, yielding alcohol. In addition to the foregoing products, we secured a considerable quantity of carbon monoxide. The initial temperature of the tests was 200°; it was then raised to 300°, the entire process taking place at the latter temperature.

Thermal decomposition of 10 g of the sodium ethyl carbonate yielded 851 ml of combustible gas, 3.21 g of liquid, and 5.40 g of a solid residue. Analysis of the gas indicated its composition to be 43.5% CO_2, 16.1% C_2H_4, and 40.4% CO. (In every case of thermal decomposition the amount of gas was computed after the volume had been reduced to standard conditions). The liquid (which had a pleasant, minty, fruity odor) was first tested with Schiff's reagent, after which it was found to contain an aldehyde. Fractionation of the liquid yielded ethyl alcohol. Analysis of the solid residue after the tarry mass was removed indicated the presence of soda.

The evolution of carbon monoxide may be due to the fact that this thermal decomposition of the sodium ethyl carbonate involves the formation of sodium formate (from the sodium lactate formed as an intermediate product). The aldehyde or the alcohol yields carbon dioxide at a higher temperature or when catalysts are present. Kuznetsov [14] succeeded in securing a small quantity of carbon monoxide from aldehydes only by the use of a catalyst – platinum black – and a temperature of 300°. The soda and the tarry and carbonized substances formed during the process of thermal decomposition may act as catalysts in the decomposition reaction.

Summing up, the decomposition of sodium ethyl carbonate may be represented as follows:

$$C_2H_5OCOONa \rightarrow HCOONa + CH_3CHO,$$

supplementing the outline of the reaction given above.

The HCOONa yields carbon monoxide and caustic soda, the latter reacting with the carbon monoxide to form soda and water, and the latter, in turn hydrolyzing the sodium ethyl carbonate. Moreover, the sodium formate may react as follows: $2HCOONa \rightarrow H_2 + (COONa)_2$. The hydrogen evolved may form ethane by reacting with the ethylene.

SUMMARY

1. A study has been made of the thermal decomposition of sodium ethyl carbonate, during which it was found that at a temperature of some 300° the decomposition of the salt proceeds in two ways: a) the formation of an unsaturated hydrocarbon (ethylene), carbon dioxide, ethyl alcohol, water, and soda. The alcohol is produced in a secondary reaction by the action of the water, evolved during the decomposition of the sodium bicarbonate, upon the sodium ethyl carbonate; and b) the formation of a large amount of carbon monoxide plus some aldehyde (in addition to the carbon dioxide, alcohol, water, soda, and tarry substances, the latter being produced as resinification products and condensation products of the aldehyde).

2. The thermal decomposition of $C_2H_5OCOONa$ may be represented as follows:

$$C_2H_5OCOONa \rightarrow Na_2CO_3 + C_2H_5OH + H_2O + C_2H_4 + CO_2$$
$$C_2H_5OCOONa \rightarrow CO_2 + CO + H_2O + C_2H_5OH + CH_3CHO + NA_2CO_3.$$

3. The carbon monoxide evolved during the thermal decomposition of the sodium ethyl carbonate is produced via an intermediate product – sodium formate – which is then further decomposed to yield carbon monoxide, rather than via an alcohol or an aldehyde.

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THE PROBLEM OF ANALYZING THE RAMAN SPECTRA OF ACETYLENIC HYDROCARBONS

A. I. Zakharova

The exceptional importance of Raman spectra in studying the structure of various organic compounds is generally admitted at the present time. In an earlier paper [1] we used this method to determine whether it is possible for methyl-tert-butylacetylene to exist, the method providing a completely unequivocal and positive answer to the question. The initial material used for the synthesis of methyl-tert-butylacetylene was tert-butylacetylene. We were interested in obtaining the raman spectrum of this latter hydrocarbon as additional material indicating its structure. As far as we have been able to learn from a search of the literature on the investigation of acetylenic hydrocarbons by means of Raman spectra, this is the first time tert-butylacetylene has been investigated by this method.

We prepared tert-butylacetylene from pinacoline as described in our previous report [1]. We used the hydrocarbon distilled into a column, with a b.p. of 39-40°; d_4^{15} 0.6741; n_D^{15} 1.37721, in our spectrographic analysis.

Raman spectrum frequencies of tert-butylacetylene: 2138 (1); 2105(5), 2050(0.5), 2011(0.5), 1623(0.5), 1451(4), 1205(3), 1023(0.5), 929(3), 887(2), 701(4), 579(2), 543(1), 362(0.5), 193(5). (See plate, page 665).

According to the data in the literature [2], the characteristic frequencies for monosubstituted acetylenes lie in the 2000-2120 cm^{-1} range. According to our data, the frequency of the acetylenic bond in tert-butylacetylene is 2105 cm^{-1}. The spectrum of tert-butylacetylene also exhibits intense lines at the frequencies of 1205 and 1451 cm^{-1}, which we noticed in the spectrum of methyl-tert-butylacetylene [1]; according to the literature [3], these frequencies are characteristic of compounds with complicated branching at the end of the chain and of the CH_3 group, respectively. The intensity of the spectrum lines was estimated visually. The brightest line in the spectrum was given the value of 5.

I wish to express my profound gratitude to Prof. G.B. Pigulevsky for his invaluable advice and assistance rendered me in conducting this research, as well as in my research on the Raman spectrum of methyl-tert-butylacetylene. I also wish to express my thanks to A.T.Ryskalchuk and S.A.Kozhina for their great interest in my research.

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RESEARCH ON ALLENE HYDROCARBONS

I. THE SYNTHESIS OF METHYLPHENYLPROPADIENE

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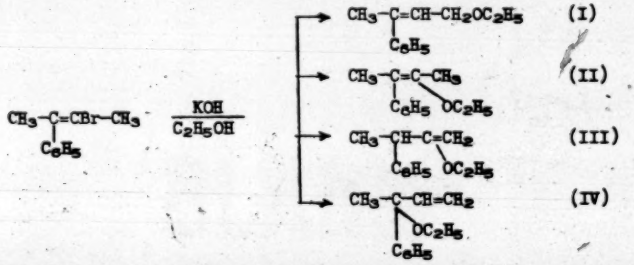
Of the unsaturated compounds with the general formula C_nH_{2n-2}, the derivatives of acetylene and butadiene have been extensively investigated and have become very important industrially, whereas the allene compounds, which are their isomers and have greatly different chemical properties, have remained within the precincts of laboratory research. Some research has been done on aliphatic allenes, chiefly the first few members of this series [1], while extremely little has been done on allenes containing aromatic radicals [2] and with an allene bond within the ring [3]. The principal factor hampering the development of the chemistry of the allenes is, no doubt, the complexity of the methods required for their preparation, which is apparently due, in turn, to the extreme instability of the allene bond. The latter circumstance, finally, is the reason behind all sorts of addition and polymerization reactions and isomeric transformations during the formation of allene compounds. One of the methods of securing these substances involves the action of an alcoholic alkali upon dihalogen-substituted saturated hydrocarbons or monohalogen-substituted unsaturated hydrocarbons.

Though this method may be used to secure aliphatic allenes, especially those with asymmetrical substituents [4], it has never been employed for the production of allenes containing aromatic radicals. Of the eight aryl-substituted allenes, [2] known in the literature, only one [5], tetraphenylpropadiene, has been prepared by reacting alcoholic KOH with α- or β-bromo-α,α,γ,γ,-tetraphenylpropene.

A.P.Golovchanskaya [6] has tried to secure a symmetrically substituted diphenylpropadiene by using an alcoholic alkali to detach 2 HBr from 1,2-dibromo-1,3-diphenylpropane. But after boiling an alcoholic solution of the bromide with an alcoholic solution of KOH for many hours, she obtained an unsaturated ether – 1,3-diphenyl-3-ethoxypropene-1 – instead of diphenylpropadiene. According to the author, the detaching of the HBr molecule and the replacement of the bromine by an ethoxy group occur practically simultaneously.

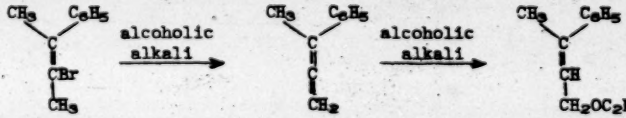
In the present research it has been our objective to secure asymmetrical methylphenylpropadiene by using an alcoholic alkali to detach a molecule of hydrogen bromide from 3-bromo-2-phenylbutene-2. The initial unsaturated bromide was produced by reacting bromine with the tertiary alcohol methylethylphenylcarbinol. In so doing we found [7] that tertiary aliphatic-aromatic alcohols with the phenyl group attached to the tertiary carbon atom are brominated as follows:

In the last stage of the reaction hydrogen bromide is detached spontaneously, even at ordinary temperature, by detaching bromine from the carbon atom to which the phenyl group is attached. The end products of the reaction are unsaturated monobromides. The weakness of the bond between bromine and a tertiary carbon atom to which phenyl is attached was also observed in the bromination of various ethylene derivatives [8], hydrogen bromide also being detached and unsaturated monobromides being formed. When 3-bromo-2-phenylbutene-2 was poured into 20% alcoholic KOH, potassium bromide was immediately thrown down quantitatively, with the evolution of some heat; as in the example cited by A.P.Golovchanskaya, we too secured a substance with the empirical formula $C_{12}H_{16}O$, which proved to be an unsaturated ether, instead of the hydrocarbon. A substance of this composition could be formed either by the detachment of a HBr molecule, giving rise to methylphenylpropadiene, to which elements of an alcohol are added, or by the substitution of an ethoxy group for the bromine. The reaction may occur in four different ways:



The structure of the resulting substance was determined by oxidizing it with a 1% solution of permanganate, the following oxidation products being found: 2-phenyl-4-ethoxybutanon-3-ol-2, $CH_3-\underset{\underset{C_6H_5}{|}}{COH}-CO-CH_2-OC_2H_5$, acetophenone, and benzoic, formic, and ethoxyacetic acids. Furthermore, the ready reduction of silver throughout the crystallization range of the silver salts of the volatile acids indicated that a readily oxidized acid was present, which in this case most likely was glyoxylic acid, formed by the oxidation of the ethoxy-acetic acid. The increased percentage of silver found for this acid was doubtless due to the presence of silver acetate, the second product of the oxidation of ethoxyacetic acid.

Thus, the oxidation products bear out the presence of a substance that conforms to Formula (I). The formation of 2-phenyl-4-ethoxybutene-2 in this case is conceivable solely as follows:



The foregoing leads us to suppose that the mechanism involved in the formation of the ether 1,3-diphenyl-3-ethoxypropene-1 synthesized by A.P.Golovchanskaya is similar to the mechanism involved in the formation of our ether.

In both experiments it is most likely that the intermediate stage of the reaction is the formation of an aryl-substituted allene, which readily adds elements of an alcohol under the reaction conditions, the hydrogen being added to

the least saturated middle carbon atom of the allene bond.

EXPERIMENTAL

Action of an alcoholic alkali upon 3-bromo-2-phenylbutene-2. The unsaturated bromide 3-bromo-2-phenylbutene-2 was prepared by brominating methylethylphenylcarbinol; its boiling point was 101-104° at 5 mm. 220 g of the bromide was added to 600 g of a freshly prepared 20% alcoholic alkali. Potassium bromide was thrown down at once, a small amount of heat being evolved. The mixture was heated for 10-15 minutes over a water bath to remove all the KBr, the liquid acquiring a reddish color. The potassium bromide was filtered out (it weighed 122 g, whereas 124 g was called for theoretically). The filtrate was diluted with water, and the substance was extracted with ether. The ether extract was washed with water and desiccated above $CaCl_2$; the ether was driven off, and the substance distilled in vacuum. Triple distillation at 2.5 mm yielded the following fractions: I - 42-60°, 13.8 g; II - 68-80°, 12.1 g; III - 80-84°, 61.3 g; IV 84-88°, 27.8 g; V 88-90°, 17.0 g; and VI - above 90°, 12.0 g of a thick oil; a total of 144.0 g.

All the fractions contained a trace of some halogen-substituted substance, and only after another three distillations at 1.5 mm did we secure a substance with a b.p. of 90.5-91° – a highly mobile liquid with a slight odor of geraniums, which decolorizes bromine rapidly and permanganate instantaneously.

d_4^{20} 0.9966; n_D^{20} 1.5382; MR_D 55.28; computed 55.06. 0.1880 g substance: 18.88 g benzene: Δt 0.278°. 0.4024 g substance: 18.88 g benzene: Δt 0.619°. Found: M 184, 177. 0.1935 g substance: 0.5709 g CO_2; 0.1467 g H_2O. 0.1696 g substance: 0.5016 g CO_2; 0.1306 g H_2O. Found %: C 80.47, 80.66; H 8.48, 8.61. $C_{12}H_{16}O$. Computed %: C 81.75; H 9.15; M 176.

The slight discrepancy between our analytical data and the computed values must be attributed to a minute trace of some substance hard to remove, which contained a halogen, traces of which were found in the tested substance.

Oxidation. 4.74 liters of a 1% solution of $KMnO_4$ was added to 33.8 g of the substance emulsified in 200 ml of water, on the basis of 2 atoms of oxygen per molecule of the substance. The permanganate was decolorized instantaneously and completely. After the solution had been saturated with CO_2 and neutralized with potash, the precipitate was filtered out. The neutral volatiles were driven off from the precipitate with steam, while the acid salts were washed out with hot water. 4 g of neutral volatiles were driven off from the filtrate over an open flame, they distilled at 7 mm. This yielded the following fractions: I - 102-112°; II - 112-122°; III - 122-127°. Treating Fractions I and II with semicarbazide yielded a semicarbazone, which melted at 197° after recrystallization from alcohol. A test mixture with the semicarbazone of acetophenone exhibited no depression of the melting point. Fraction III, as well as the substance driven off from the MnO_2 precipitate by steam, were not analyzed, owing to their minute quantities. After the neutral volatiles had been driven off, the neutral nonvolatiles, totaling 7.0 g, were extracted with ether. They were desiccated above Na_2SO_4, then distilled at 1 mm. The following fractions were secured: I - 90-111.5°, 0.5 g; II - 111.5-112.5°, 5.0 g; and III - above 112.5°, 0.5 g. Fraction II was a liquid with a slight odor of tertiary alcohols, which decolorized permanganate rapidly and contained active hydrogen. Its analysis yielded the following results:

$d_4^{18.5}$ 1.0900; $n_D^{18.5}$ 1.5170; MR_D 57.72; computed 57.19. 0.1444 g substance; 22.05 g benzene: Δt 0.172°. 0.3093 g substance: 22.05 g benzene: Δt 0.323°. 0.1125 g sub.: 12.05 ml CH_4 (0°, 760 mm). 0.1279 g substance: 17.38 ml CH_4 (0°, 760 mm). 0.2021 g substance: 0.5141 g CO_2, 0.1483 g H_2O. Found %: C 69.38; H 8.22. M 191, 223; OH 8.15, 8.25. $C_{12}H_{18}O_3$. Computed %: C 69.2; H 7.75; M 208; OH 8.17.

When reacted with semicarbazide, this substance formed a semicarbazone that melted at 162-163°. The residue left after the neutral nonvolatiles had been removed was acidulated with sulfuric acid, and the volatile acids were driven off. The solution of volatile acids was neutralized with potash, and concentrated by evaporation; the salts were decomposed with sulfuric acid, and the volatile acids were driven off again, after which they were heated with silver carbonate. This produced a copious black precipitate and a beautiful silver mirror – an indication of the presence of formic acid. Inasmuch as silver was being reduced throughout the concentration of the silver salts over the water bath (formation of the mirror), evaporation was carried out above sulfuric acid in a vacuum desiccator. Five silver-salt fractions were secured:

I - 0.1529 g substance: 0.0940 g Ag; II - 0.0789 g substance: 0.0494 g Ag; III - 0.1933 g substance: 0.1196 g Ag; IV - 0.0968 g substance: 0.0549 g Ag; V - 0.1972 g substance: 0.1005 g Ag. Found %: Ag 61.48, 62.57, 61.87, 56.71, 50.96. $C_4H_7O_3Ag$, Computed %: Ag 51.15. C_2HO_3Ag computed %: Ag 59.63. $C_2H_3O_2Ag$, computed %: Ag 64.64.

Thus, analysis of the silver salts of the volatile acids indicates the presence of ethoxyacetic acid and, most probably, of glyoxylic acid with a trace of acetic acid. The nonvolatile acids were extracted with ether. Recrystallization yielded a substance with a m.p. of 121°, which sublimed and possessed the properties of benzoic acid. A test sample mixed with benzoic acid exhibited no depression of the melting point.

SUMMARY

When an alcoholic alkali is reacted with 3-bromo-2-phenylbutene-2, a molecule of hydrogen bromide is evolved, and gem-methylphenylpropadiene is most likely formed, it adding elements of an alcohol under the reaction conditions and yielding 2-phenyl-4-ethoxybutene-2.

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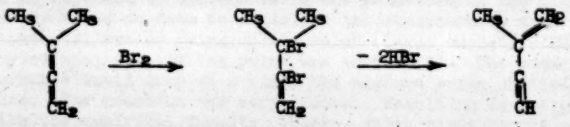
RESEARCH ON ALLENE HYDROCARBONS

II. THE ADDITION OF BROMINE TO AS-DIMETHYLPROPADIENE

V. I. Pansevich-Kolyada

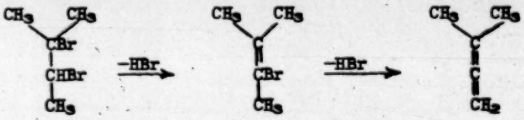
The chemical properties of allene hydrocarbons are governed by their possessing two consecutive double bonds, with radicals adjoining these bonds. The nature of the radicals and their position within the hydrocarbon molecule determines the asymmetry of the molecule and the inequality (and, hence, the different chemical activity) of the carbon atoms at the allene bond. Apparently bearing in mind this property of allene compounds, A.E.Favorsky and K.I.Debu [1] tried to prepare Reboul's vallylene by adding a molecule of bromine to asymmetrical dimethylallene and then detaching two molecules of hydrogen bromide from the resulting dibromide. The authors expected the second and third carbon atoms to be highly active, and that the bromine would therefore be added at the 2,3 positions:



But instead of getting Reboul's vallylene, they secured an unsaturated ether $C_5H_7OC_2H_5$, the formation of which A.E.Favorsky pictured as follows:

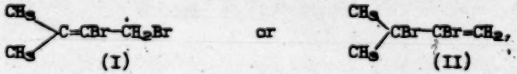
S.V.Lebedev attributes [2] the polymerization processes of allene hydrocarbons to the differing saturation of the allene-bond carbon atoms. The dimers he produced – the initial polymerization products – demonstrate that in the asymmetrically substituted allenes this process takes place chiefly at the double bond between the central carbon atom and the more highly hydrogenated carbon atoms. We found this same pattern of behavior in our effort to produce asymmetrically substituted methylphenylpropadiene by letting an alcoholic alkali react with 3-bromo-2-phenylbutene-2 [3]. Instead of the hydrocarbon, we got the unsaturated ether $CH_3-\underset{\displaystyle C_6H_5}{\underset{|}{C}}=CH-CH_2-OC_2H_5$ as the result of the addition of elements of an alcohol at the same position to the methylphenylpropadiene – the intermediate reaction product. Lastly, different amounts of energy are expended in the formation of cumulative double bonds in asymmetrically substituted allene hydrocarbons, and this must doubtless be reflected in their differing chemical activity.

As we know, the synthesis of asymmetrical di- and trisubstituted aliphatic allenes by reacting dibromides with an alcoholic alkali takes place in two stages [4]:



The first HBr molecule is detached readily, while detaching the other requires heating to 140-150° under pressure. This leads us to think that of the two double bonds, the bond formed during the second stage must be more active, for more energy was required to form it, and that the transition from allene hydrocarbons to the bromides by attaching halogens or hydrohalic acids to the former will be effected by a process that is the reverse of the production of the allene bond. There is no doubt, however, that the only way to find out whether this supposition applies to all compounds of the allene series is by experiment. There are no researches listed in the literature dealing with a study of the comparative chemical activity of the double bonds in allene hydrocarbons; we therefore took it as our objective to shed some light on this interesting problem of allene chemistry, using several examples in our study.

We determined to begin our research with dimethylallene, as the first member of the asymmetrical disubstituted allenes and also because the 1,2-dibromo-3-methylbutene-2 we expected to synthesize is not described in the literature, while A.E.Favorsky cites no data to establish the structure of this substance. We prepared dimethylallene by using an alcoholic alkali to detach 2HBr from 2,3-dibromo-2-methylbutane; its boiling point was 40.5-42.5°. The bromine was added to the hydrocarbon a small drop at a time, the mixture being chilled with a snow-and-salt mixture. The reaction was very violent, resulting in the preparation of a substance with the empirical formula $C_5H_8Br_2$, which might be one of the following isomers:



Oxidation of the bromide with permanganate yielded acetone and formic, acetic, and bromoacetic acids as oxidation products. The formation of bromoacetic acid confirmed the first of the two formulas for the synthesized substance. Hence, when bromine is added to as-dimethylallene, the first halogen molecule is added at the 1,2-position, giving rise to 1,2-dibromo-3-methylbutene-2.

EXPERIMENTAL

Dimethylallene was prepared by detaching 2HBr from 2,3-dibromo-2-methylbutane with an alcoholic alkali. The detaching of the first molecule of HBr was carried out in a flask fitted with a reflux condenser. The resulting unsaturated monobromide boiled at 117-121°. d_4^{20} 1.3073; n_D^{20} 1.4642; MR_D 31.44. Computed 32.58.

The second molecule of HBr was detached by heating the substance to 140-150° for 12 hours in sealed glass tubes. The resulting 3-methylbutadiene-1,2 had a boiling point of 40.5-42.5°.

7 g of bromine was added drop by drop to 3 g of dimethylallene, chilled with a snow-and-salt mixture, allowing one molecule of bromine per molecule of the hydrocarbon. Each drop of bromine entered into reaction with a crackling sound. This yielded a light, mobile, yellowish liquid with the odor of rotting weeds. It decolorized a permanganate solution instantaneously. The bromination product was desiccated above $CaCl_2$ and then 9.5 g of it was distilled at 47 mm. The

following fractions were collected: I) 41.5-52.5°, 1.0 g; II) 52.6-109.0°, 1.5 g; III) 109.5-114°, 2.5 g (most of this fraction boiled at 111-112°); IV) 114-143°, 1.5 g; and V) 1.5 g of tar.

Analysis of Fraction III: d_4^{20} 1.7702; n_D^{20} 1.5479; MR_D 40.88. Computed 40.35. 0.2334 g substance: 0.3800 g AgBr. Found %: Br 69.28. $C_5H_8Br_2$, computed %: Br 70.15.

Oxidation. 200 ml of a 2% solution of $KMnO_4$ was added, with chilling with snow and water and vigorous shaking, to 2.9 g of the substance in 150 ml of water. The first half of the permanganate was decolorized very quickly, though the color of the second half disappeared with difficulty; oxidation was subsequently performed at room temperature because of this. The last batch of permanganate was not decolorized. The whole was heated over a water bath for 30 minutes, and, as it was not completely decolorized, the excess $KMnO_4$ was reduced with hydrogen peroxide. After saturation with CO_2 and neutralization with potash, the precipitate was filtered out and treated three times with hot water. The aqueous extracts were combined with the filtrate, and the neutral volatile substances were driven off over a naked flame. The first runnings smelled of acetone, with a trace of the slightly fruity odor of acetaldehyde, and formed a silver mirror. The distillate of neutral volatiles was treated with aqueous silver oxide and then redistilled. The distillate smelled of acetone and yielded a semicarbazone with a m.p. of 187-188° when treated with semicarbazide. A test sample, mixed with the semicarbazone of acetone, exhibited no depression. The residue left after the neutral volatiles had been driven off was acidulated with sulfuric acid, and the volatile acids were driven off. The distillate displayed an acid reaction to the very end. The distillate was heated with silver oxide. A black precipitate was thrown down – indicating the presence of formic acid, after which a silver mirror was formed. The precipitate was filtered out, but when the solution was concentrated, silver was again reduced. Evaporation in a vacuum desiccator yielded 3 fractions of white crystals:

I) 0.0540 g substance: 0.0345 g Ag. Found %: Ag 63.9. $C_2H_3O_2Ag$, computed % Ag 63.64; II) 0.0821 g substance: 0.0451 g Ag. Found %: Ag 54.9; III) 0.0785 g substance: 0.0345 g Ag. Found %: Ag 43.95. $C_2H_2O_2BrAg$. Computed %: Ag 43.89.

SUMMARY

In brominating 3-methylbutadiene-1,2, the first bromine molecule is attached at the 1,2-position, constituting 1,2-dibromo-3-methylbutene-2.

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RESEARCHES ON α-KETONIC ETHERS

IV. THE HYDROGENATION OF α-KETONIC ETHERS AS A METHOD OF PREPARING α-KETOLS

T. I. Temnikova and V. A. Kropachev

In earlier papers of this research series we described a new and simple way of preparing aliphatic-aromatic α-ketonic ethers [1], and used it to develop [2,3] a new method of synthesizing individual α-ketols. Using palladium catalysts, we managed to synthesize the first samples of α-ketols containing a benzyl group by hydrogenating the α-keto ethers under very mild conditions. In particular, we synthesized: $C_6H_5-CH_2-CHOH-CO-CH_3$ (I), benzylacetylcarbinol, and $C_6H_5-CH_2-CHOH-CO-C(CH_3)_3$ (II), benzyltrimethylacetylcarbinol.

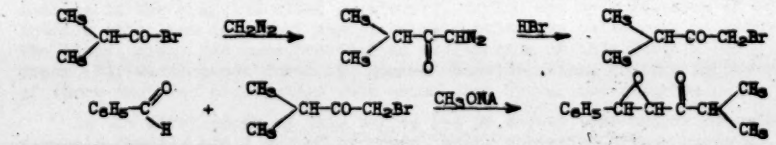
The synthesis and investigation of two other α-ketols: $C_6H_5-CH_2-CHOH-CO-CH_2-CH_3$ (III), benzylpropionylcarbinol, and $C_6H_5-CH_2-CHOH-CO-CH(CH_3)_2$ (IV), benzylisobutyrylcarbinol, are described in the present paper. These α-ketols were prepared by the same method; they complete the series of aliphatic-aromatic α-ketols containing benzyl radicals, with the general formula:

$C_6H_5-CH_2-CHOH-CO-R$, where R = CH_3, C_2H_5, $CH(CH_3)_2$ and $C(CH_3)_3$.

Both of the ketonic ethers required for this research – ethyl styryl ketonic ether (Table 1, No. 2) and isopropyl styryl ketonic ether (Table 1, No. 3) – were prepared by condensing benzaldehyde with the respective α-halogen ketones.

The method of preparing the ethyl styryl ketonic ether differed in no way from the methods described previously [1].

The isopropyl styryl ketonic ether, prepared for the first time in the following manner:



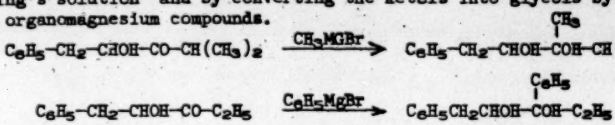
is a nearly colorless liquid with a b.p. of 116.5-117.5° at 1 mm. The substance exhibits all the reactions and the semicarbazone that are typical of α-ketonic ethers.

Catalytic Hydrogenation of α-Ketonic Ethers

In our previous paper [3] we commented on the selective hydrogenation of aliphatic-aromatic α-ketonic ethers. We learned that when α-ketonic ethers are hydrogenated under extremely mild conditions in alcoholic or ether solutions, the nature of the process can be changed, according as we use Pt or Pd as catalysts.

In the present paper we show that isopropyl styryl ketonic ether is not hydrogenated when Pt is used as a catalyst. When ethyl styryl ketonic ether and iso-

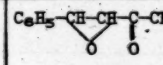
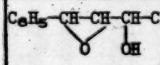
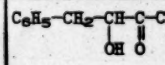
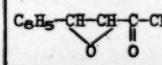
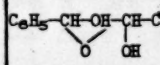
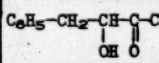
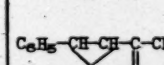
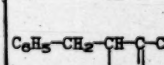
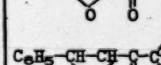
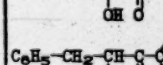
propyl styryl ketonic ether are hydrogenated above Pd/Ni, 1 mol of H_2 is smoothly and quantitatively added, giving rise to the respective α-ketols. The fact that the reaction is carried to completion in one direction was proved by the quantitative determination of the percentage of the α-ketol in the resulting substance with Fehling's solution* and by converting the ketols into glycols by reacting them with organomagnesium compounds.



The ketols and glycols synthesized in this research have not been described in the literature.

Thus, the present research has demonstrated that the selectivity of hydrogenation observed in our earlier research [1] is a general pattern of behavior for the aliphatic-aromatic α-ketonic ethers. The data obtained in this research are listed in Table 1.

TABLE 1

No.	Initial ketonic ether	Hydrogenation product		References
		With platinum	With palladium	
1				[1,3]
2				[1] and the present research
3		Not hydrogenated		The present research
4		Not hydrogenated		[2]

The conclusion reached in our previous paper [3] concerning the sequence in which the oxide ring is ruptured during catalytic hydrogenation is likewise borne out: as in the examples cited previously, during the hydrogenation of ethyl styryl ketonic ether and isopropyl styryl ketonic ether the oxide ring is ruptured at the phenyl ring. We have provided an explanation of this fact in our preceding paper [3]; we also set forth the general considerations concerning the rupture of three-membered oxide rings when acted upon by various reagents.

In the first paper of this series [1] we showed that oxides of unsaturated alcohols readily add 1 mol of hydrogen, being converted into α-glycols.

The α-ketols we have synthesized behave differently. The sharply selective nature of the hydrogenation of α-ketonic ethers with palladium catalysts enabled us to assume that the α-ketols formed as the result of hydrogenation could not be hydrogenated any further. Special experiments showed that α-ketols containing a benzyl radical could not be hydrogenated with Pt black or with Pd/Ni. Endeavors to hydrogenate benzylacetylcarbinol (I) and benzylpropionylcarbinol (III) with Pt black met with failure.

Hydrogenation of these α-ketonic ethers with palladium catalysts always ended

*The percentages of 94.5 and 95.1 we secured are apparently too low, as in our previous experiments [3], since boiling ketols in an alkaline medium may result in their partial condensation, cleavage, etc.

after 1 mol of hydrogen had been absorbed. Adding more catalyst caused no further absorption of hydrogen; introducing additional batches of the ketonic ether always resulted in the absorption of 1 molar equivalent of hydrogen.

EXPERIMENTAL

The ethyl styryl ketonic ether was prepared by the T.I.Temnikova and V.F. Martynova method [1].

Isopropyl Styryl Ketonic Ether

This ether was prepared by condensing bromomethyl isopropyl ketone with benzaldehyde.

Preparation of bromomethyl isopropyl ketone.* 14.5 g of isobutyrl bromide was slowly added, drop by drop, while the reaction vessel was chilled with ice (the solution's yellow color soon changes to green) to an ether solution of diazomethane (CH_2N_2), prepared by decomposing N-nitrosomethylurea. A current of anhydrous hydrogen bromide was then passed through the ether solution. The current of HBr was turned off when a sample of the solution began to fume when exposed to the air. The mixture was allowed to stand for 1 hour at 0°. The ether solution was washed with water and then washed (twice) with a solution of soda and desiccated above $MgSO_4$. Driving off the ether left a substance that was distilled in vacuum. a 84-86° fraction was collected at 50 mm; n_D^{20} 1.4678. Yield 74%.

Preparation of isopropyl styryl ketonic ether. A solution of sodium methoxide (2.15 g of sodium) in 50 ml of methanol was slowly added, drop by drop, during the course of 2 hours, with chilling to 5° and vigorous stirring, to a mixture of 13 g of benzaldehyde, 15.7 g of bromomethyl isopropyl ketone (b.p. 84-86°), and 10 ml of methanol. Stirring was continued for 1 hour after all the sodium methoxide had been added. The mixture, which had a neutral reaction and a penetrating odor (traces of the bromoketone), was poured into water that had been slightly acidulated with acetic acid; an ether extract was made, and the latter was washed with a weak solution of potash. It was then desiccated above $MgSO_4$. The ether was driven off, and the product was double-distilled in vacuum.

Isopropyl styryl ketonic ether is a nearly colorless liquid with a faint odor. The yield was 65%.

B.p. 116.5-117.5° at 1 mm: d_4^{20} 1.055; n_D^{20} 1.5180; MR_D 54.64. Computed 53.60.

0.1497 g substance: 0.4112 g CO_2; 0.1040 g H_2O. 0.0684 g substance: 0.1881 g CO_2; 0.0047 g H_2O; 0.1358 g substance; 17.15 g benzene: Δt 0.208°; 0.2255 g substance; 17.15 g benzene: Δt 0.352°. Found %: C 75.09, 75.00; H 7.79, 7.97; M 194.4, 192.0. $C_{12}H_{14}O_2$. Computed %: C 75.76; H 7.42; M 190.23.

Qualitative reactions: it liberates iodine from a solution of potassium iodide in acetic acid; it does not evolve methane when treated with methylmagnesium iodide; Fehling's solution oxidizes it only when heated.

The semicarbazone of isopropyl styryl ketonic ether was prepared in the usual manner. It's m.p. was 77-86° after recrystallization from methanol. The solution turns yellow when it is refined by recrystallizing it from ethyl alcohol. The crystallized substance does not melt sharply, though it decomposes. The determination was made in sealed capillaries. The m.p. is 126-131° when gradually heated, but 137-140° when heated rapidly.

0.1010 g substance: 14.4 ml N_2 (22°, 760.8 mm). Found %: N 16.41. $C_{13}H_{17}N_3O_2$. Computed %: N 16.99.

*We print a description of this synthesis because the original paper [4] gives merely brief indications of the general method involved in the preparation of bromomethyl ketones, and not the synthesis of the compound we are interested in. Moreover, this is still the sole method for the preparation of individual halogen methyl ketones without traces of isomeric halogen ketones.

Hydrogenation of Isopropyl Styryl Ketonic Ether

1. Hydrogenation with Platinum

Experiment 1. 1.9 g of isopropyl styryl ketonic ether, 0.14 g of platinum black, 30 ml of absolute alcohol. 6 ml of hydrogen was absorbed in 50 minutes of agitation in a "duck". The absorption of 1 mol of H_2 would require 245 ml.

0.6 g of allyl alcohol in 10 ml of absolute ether was poured into the same "duck". Hydrogenation set in at once at an initial rate of 8-9 ml per minute. 252 ml of hydrogen was absorbed in 33 minutes (249 ml being required for 1 mol of H_2).

Experiment 2. 1.9 g of isopropyl styryl ketonic ether in 30 ml of absolute ether with 0.21 g of another sample of platinum black. Practically no hydrogen was absorbed (3 ml in 20 minutes).

2. Hydrogenation with Pd/Ni

Experiment 1. 1.9 g of the ketonic ether (0.01 mol), 0.5 g of nickel; 0.5 ml of catalyst (equivalent to 0.05 g of $PdCl_2 \cdot 2NaCl$); 30 ml of ethyl alcohol, t 14.5°, p. 763 mm. 1 H_2 represents 234 ml.

TABLE 2

T	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	25
V	18	54	91	128	158	185	207	218	223	224.5	226	227.5	229	229.5	230	233
v	18	36	37	37	30	27	22	11	5	1.5	1.5	1.5	1.5	0.5	0.5	3

Notes: T = time, minutes; V = ml of hydrogen absorbed in time T; v = ml of hydrogen absorbed between readings.

Experiment 2. In the hydrogenation of 3.8 g of the ketonic ether in 30 ml of ethyl alcohol with 1 g of Ni and 1 ml of catalyst (0.1 g $PdCl_2 \cdot 2NaCl$), 470 ml of hydrogen was absorbed in 7 minutes.

The hydrogenation product of isopropyl styryl ketonic ether was recovered in the usual manner: the catalyst was filtered out, and the alcohol was driven off in vacuum. The residue of 5.5 g was distilled. This yielded the following fractions: up to 111° (1.5 mm), 1 drop; 111-112° (1.5 mm), 4.2 g (Yield = 75%).

The resulting substance is a slightly greenish liquid (b.p. 125° at 4 mm) that reduces Fehling's solution.

d_4^{20} 1.035; n_D^{20} 1.5106; MR_D 55.62; computed 55.55.
0.1286 g substance: 0.3531 g CO_2; 0.0970 g H_2O. 0.0997 g substance: 0.2734 g CO_2; 0.0757 g H_2O. 0.1323 g substance: 16.55 g benzene: Δt 0.216°; 0.3154 g substance; 16.55 g benzene: Δt 0.480°. 0.1304 g substance: 16.42 ml CH_4 (14.5°, 768 mm) [5]. Found %: C 74.88, 74.79; H 8.44, 8.49; M 190.4, 203.9; active H 1.03. $C_{12}H_{16}O_2$. Computed %: C 74.96; H 8.39; M 192.3; active H 1.

Quantitative determination of the percentage of the α-ketol by means of Fehling solution [6]. This determination was made simultaneously in two 200-ml Erlenmeyer flasks, fitted with reflux condensers. A mixture of 10 ml of a $CuSO_4$ solution (69.28 g per liter), 10 ml of an alkaline solution of Seignette salt (344 g + 100 g NaOH per liter), and 20 ml of water was heated for 10 minutes. An ampoule with a weighed quantity of the ketol had been placed in one of the flasks beforehand. After heating was complete, the flasks were cooled with a jet of water, and 10 ml of 30% KI and 25% H_2SO_4 was added to each of them. The iodine liberated was titrated back with hyposulfite and starch.

Experiment 1. 0.1451 g sugstance: required 12.1 ml hyposulfite solution (T = 0.02398 g/ml). Blank test – 26.9 ml hyposulfite. Found %: ketol 94.7.

Experiment 2. 0.1593 g substance: required 10.6 ml of hyposulfite. Blank test – 26.8 ml hyposulfite. Found %: 95.1% ketol.

The semicarbazone was prepared in the usual manner and was recrystallized from dilute methanol (1:1). Colorless, dense, sparkling crystals shaped like elongated prisms. M.p. 136.5-137.5°.

0.1007 g substance: 14.8 ml N_2 (22°, 764.4 mm); 0.1102 g substance: 16.1 ml N_2 (22°, 764.4 mm). Found %: N 16.78, 16.70. $C_{13}H_{19}N_3O_2$. Computed %: N 16.86.

We were unable to secure the p-nitrophenylhydrazone or osazone. A vaseline-like mass was formed, which rapidly resinified. In one of our tests, letting a mixture of the substance with p-phenylhydrazine acetate stand for a long time yielded reddish-orange crystals, which we were unable to recrystallize, however, as this caused them to resinify.

Nor could we secure a phenylosazone.

Preparation of 2,3-Dimethyl-5-phenylpentanediol-3,4

1.95 g of benzylisobutyrylcarbinol in 12 ml of absolute ether was added drop by drop, with constant stirring and chilling with ice, to an ether solution of methylmagnesium bromide, prepared from 0.8 g of magnesium. Then the mixture was allowed to stand for an hour at room temperature. Two layers formed. The mixture was heated, with constant stirring, until the ether boiled gently for 4.5 hours and then was set aside to stand overnight. The coordination compound was decomposed carefully with water until a gradual mass resulted. The ether layer was removed. The magnesium salts were triturated with ether, and the ether extract was added to the ether layer. After the latter had been desiccated above $MgSO_4$, the ether was driven off over a water bath, the residual ether being driven off in vacuum. The residue solidified into a lumpy white mass. Yield: 89%. Recrystallization from petroleum ether (b.p. 60-80°) yielded minute acicular white crystals. M.p. 101.5-102.5°.

0.1088 g substance: 0.2962 g CO_2; 0.0946 g H_2O. 0.0800 g substance, 0.2180 g CO_2; 0.0707 g H_2O. 0.0737 g substance; 17.98 g benzene: Δt 0.101°. 0.1758 g substance: 17.98 g benzene: Δt 0.223°. 0.0946 g substance: 21.1 ml CH_4 (14.5°, 767 mm). Found %: C 74.25, 74.32; H 9.73, 9.89; M 208.2, 224.9; active H 1.96 $C_{13}H_{20}O_2$. Computed %: C 74.48; H 9.68; M 208.29; active H 2.

Oxidation of the glycol with lead tetracetate. 0.6 g of the glycol was heated to 50-60° over a water bath with 1.6 g of lead tetracetate in 5 ml of glacial acetic acid, the mixture being stirred constantly. After the tetracetate crystals had disappeared, the solution was cooled with constant stirring. A saturated solution of potash (12 g) was added to the mixture. The volatile product entrained by a current of CO_2 was collected in a solution of p-nitrophenylhydrazine acetate. A crystalline precipitate was soon thrown down. The recovered substance, which was recrystallized from dilute methanol, melted at 102-103° and exhibited no depression when mixed with the known p-nitrophenylhydrazine of methyl isopropyl ketone. An alkaline mixture of the distillate with water yielded some more of the methyl isopropyl ketone, which was likewise identified by its p-nitrophenylhydrazone.

The residue (after filtration, evaporation, and acidulation) yielded a small amount of a crystalline acid, which proved to be benzoic acid (identified by a mixed fusion sample.

Hydrogenation of Ethyl Styryl Ketonic Ether with Pd/Ni

Experiment 1. 1.76 g of the ketonic ether (0.01 mol); 1.0 g of nickel; 1.0 ml of the catalyst (0.1 g $PdCl_2 \cdot 2NaCl$); 30 ml of ethyl alcohol; t 17°; P 770 mm. The addition of 1 mol of H_2 requires 236 ml; 237 ml were absorbed in 7 minutes (Table 3).

TABLE 3

t	1	2	3	4	5	6	7	8	9	10	11	12	13	14
V	48	95	141	188	230.5	235	237	239	240	241	242	243	243.5	243.8
v	48	47	46	47	42.5	4.5	2.0	2.0	1.0	1.0	1.0	1.0	0.5	0.3

Experiment 2. 3.5 g of ethyl styryl ketonic ether; 50 ml of ethyl alcohol; 1 g of nickel; 0.1 g $PdCl_2 \cdot 2NaCl$; t 18°; P 763 mm. Absorption of 1 mol of H_2 requires 472 ml. 483 ml was absorbed in 10 minutes.

After hydrogenation the solution was poured out of the "duck", taking care not to uncover the catalyst. The catalyst was washed with 10 ml of alcohol, and the alcohol was also decanted from the catalyst. A solution of 1.5 g of ethyl styryl ketonic ether in 30 ml of alcohol was poured into the "duck". Hydrogenation was somewhat slower than in Experiment 1 and was practically completed after one mol of hydrogen had been absorbed.

After 6.4 g of the ether had been hydrogenated with Pd/Ni, the catalyst was filtered out, and the alcohol was driven off in vacuum, the residue constituting a greenish liquid containing a small amount of minute NaCl crystals. 25-30 ml of water was added, an ether extract was made, and the ether was driven off after the extract had been desiccated over $MgSO_4$. The residual greenish-yellow substance was vacuum-distilled from a small flask connected to a short dephlegmator (stub thermometer). Fraction (I) 113-116° (4 mm), 0.4 g; Fraction (II), 116.5° (4 mm), 5.1 g. The first distillate drops are greenish, later becoming colorless.*

The resultant substance is an oily colorless liquid with a distinctive odor. B.p. 116-116.5° (at 4 mm). Yield: 78-84%.

d_4^{20} 1.0619; n_D^{20} 1.51650; MR_D 50.55; computed 50.60.

0.1230 g substance; 0.3340 g CO_2; 0.0902 g H_2O. 0.1393 g substance; 0.3774 g CO_2; 0.1029 g H_2O. 0.1443 g substance; 18.25 g benzene: Δt 0.220°. 0.2338 g substance; 18.25 g benzene: Δt 0.350°. 0.1734 g substance; 19.4 ml CH_4 (15°, 781.5 mm) [5]. Found %: C 74.06, 73.91; H 8.21, 8.27; M 184.3, 187.7; active H 1.05. $C_{11}H_{14}O_2$. Computed %: C 74.11; H 7.92; M 178; active H 1.

The semicarbazone of benzylpropionylcarbinol was prepared in the usual manner. It was recrystallized from ethyl alcohol. M.p. 149-149.5°.

0.0993 g substance: 15.4 ml N_2 (17°, 766 mm); 0.1099 g substance; 17.7 ml N_2 (20°, 740 mm). Found %: N 18.25, 18.06. $C_{12}H_{17}N_3O_2$. Computed % N 17.87.

Qualitative determination of the percentage of ketol.

Experiment 1. 0.1253 g substance: required 12.8 ml of hyposulfite; blank test - 26.8 ml of hyposulfite. Found: 96.1% ketol.

Experiment 2. 0.1468 g substance: required 10.3 ml. Blank test - 26.8 ml. Found: 95.6% ketol. (titer of the hyposulfite: 0.02398 g/ml).

Preparation of 1,3-diphenylpentanediol-2,3

A solution of 7.3 g of benzylpropionylcarbinol in 60 ml of absolute ether

*Fraction one is a fairly pure α ketol, since it yielded a high percentage of semicarbazone.

was added drop by drop, with constant stirring and chilling with ice, to an ether solution of phenylmagnesium bromide, prepared with 6.5 g of magnesium. Then the reaction mixture was heated for 5.5 hours to the point at which the ether boiled gently. The mixture was left to stand overnight. The coordination compound was decomposed with water, chilled to 0°, and stirred until a granular mass was formed. The ether solution was decanted from the basic magnesium salts, which were triturated with ether, the ether extract being combined with the bulk of the solution. The ether solution was then washed with water and desiccated with $MgSO_4$. The ether was driven off, the residual mass was distilled with steam until no more emulsion was driven off, in order to get rid of the benzene and diphenyl. An ether extract was made of the residue in the distilling flask; the extract was then desiccated over $MgSO_4$, and the ether driven off. The residue was a yellow oil, which soon hardened into a solid white mass. The substance was recrystallized from petroleum ether and constituted minute white acicular crystals with a m.p. of 83.5-84.5°. Yield: 76%.

0.1188 g substance: 0.3462 g CO_2; 0.0848 g H_2O; 0.0887 g substance; 0.2592 g CO_2; 0.0644 g H_2O. Found %: C 79.52, 79.74; H 7.99, 8.12. $C_{17}H_{20}O_2$. Computed %: C 79.65; H 7.86.

Oxidation of 1,3-diphenylpentanediol-2,3 with lead tetracetate. We used 11 g of lead tetracetate in 30 ml of acetic acid and 2.5 g of the glycol in this oxidation. The reaction was carried out as described previously (cf. p. 559). The products entrained by a CO_2 current were collected in an aqueous-alcoholic solution; they did not yield a semicarbazone.

The alkaline solution was distilled with steam. After extraction with ether, desiccation above $MgSO_4$, and driving off of the ether, the substance was distilled. It proved to be an oily liquid with the odor of a ketone. B.p. 216-218°. The semicarbazone of this ketone, with a m.p. of 174-175°, exhibited no depression when mixed with the semicarbazone of known ethyl phenyl ketone.

Nothing but benzoic acid was recovered from the alkaline layer after it had been acidulated.

SUMMARY

1. Isopropyl styryl ketonic ether, not previously described in the literature, has been synthesized by condensing benzaldehyde with bromomethyl isopropyl ketone.

2. It has been shown that the method of hydrogenating aliphatic-aromatic α-ketonic ethers dissolved in ethyl alcohol with palladium catalysts, previously proposed by us, is a method generally applicable to the synthesis of aliphatic-aromatic α-ketols. By the use of this method we have synthesized and identified for the first time:

a) Benzylpropionylcarbinol.

b) Benzylisobutyrylcarbinol.

3. The addition of hydrogen to aliphatic-aromatic α-ketonic ethers in the presence of palladium (Pd/Ni; Pd black) is sharply selective; one mol of hydrogen is added, after which hydrogenation ceases.

4. Isopropyl styryl ketonic ether is practically not hydrogenated at all with Pt black.

5. Practically no hydrogen is added to α-ketols containing a benzyl radical when Pt black or Pd/Ni is used as a catalyst.

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*See CB translation p. a-541 ff.

REACTIONS WITH RADSIWANOWSKI $AlCl_3$.

CONDENSATIONS OF BENZENE WITH ALIPHATIC MONOHALOGEN DERIVATIVES

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In our previous researches we investigated the action of Radsiwanowski $AlCl_3$ (abbreviated to $AlCl_3$-R) upon mono- and dihalogen derivatives of benzene, and also traced the condensation of benzene with ethyl bromide and some polyhalogen derivatives of the aliphatic series. In the present paper we set forth the results of investigations of the condensation of benzene with methyl iodide and with isopropyl, isobutyl, and isoamyl chlorides and bromides. Moreover, we have made a series of tests of the condensation of benzene with chloroform in order to ascertain the feasibility of employing $AlCl_3$-R in condensations with polyhalogen alkyls. Collation of the results obtained under various conditions enabled us to draw several conclusions that are lacking in Radsiwanowski's papers. All the foregoing condensations are effected readily with 2-4% Al instead of equimolar quantities of ordinary aluminum chloride, at ordinary temperature and lasting 0.5 to 3 hours.

Condensations with monohalogen alkyls occur as follows:

$$C_6H_6 + RX \longrightarrow C_6H_5R + HX,$$

but, as in the Friedel-Crafts reaction, they are accompanied by the formation of polyalkylbenzenes, the isomerization of the reaction products, and by cracking reactions. A Friedel-Crafts [2] reaction of benzene with methyl iodide in the presence of 33% $AlCl_3$ does not take place in the cold or with the application of heat. Only at a pressure of 1.5 atm. and a temperature of 80-90° did the authors observe the evolution of HI and the formation of products that had boiling points ranging from 78 to 135°. We have not found any other references in the literature to this reaction. This reaction takes place with great ease under Radsiwanowski conditions, which testifies to the very high activity of the catalyst compared to ordinary aluminum chloride, which we have commented on earlier. The reaction rate is not high at room temperature, but it is vigorous and thoroughgoing at 40°, yielding a mixture of all the methylated benzenes – from toluene to hexamethylbenzene inclusive. Increasing the Al% in the reacting system promotes greater methylation. An increase in the mol fraction of methyl iodide in the CH_3I-C_6H_6 mixture favors the formation of penta- and hexamethylbenzenes, while the yield of toluene and the xylenes is diminished. We secured the maximum yield of hexamethylbenzene (11.4% of the theoretical) from a 1:3 mixture of methyl iodide and benzene. It may be that a further increase in the proportion of CH_3I would make it possible to raise the yield of hexamethylbenzene still higher, but we made no such experiments. The condensation was accompanied by the evolution of iodine.

The results obtained under various conditions with chloro and bromo alkyls enabled us to set up interesting patterns of behavior. The yields of the monoalkyl benzenes, which are the primary reaction products, drop off as the molecular weight of the radicals increases, products of deeper condensation being formed. Thus, the following yields were secured for various chloro and bromo

alkyls (all experiments were run under comparable conditions: $C_6H_6/RX = 1/0.25$ with the mixture boiled for 3 hours)(Table 1).

TABLE 1

Initial RCl	C_6H_5R, % of the theoretically possible)	High boiling products, % of the condensate	Initial RBr	C_6H_5R, % of the theoretically possible	High boiling products, % of the condensate
iso-C_3H_7Cl	57	33	iso-C_3H_7Br	53	30
iso-C_4H_9Cl	26	52	iso-C_4H_9Br	18	47
iso-$C_5H_{11}Cl$	20	53	iso-$C_5H_{11}Br$	19	51

We see from Table 1 that the use of bromo alkyls always lowered the yields of the alkyl benzenes somewhat. The quantity of catalyst used affected the course of the reaction and the extent of condensation differently. Experiments run under identical conditions showed that raising the Al per cent from 2 to 8% increased the output of amylbenzene, had only a slight effect upon the yield of propylbenzene, and reduced the output of butylbenzene.

TABLE 2

Initial chloride	Amount of aluminum (% of benzene)					
	2%		4%		8%	
	C_6H_5R, % of theoretically possible	High boiling products	C_6H_5R, % of theoretically possible	High boiling products	C_6H_5R, % of theoretically possible	High boiling products
iso-C_3H_7Cl	53	29	50	35	49	39
iso-C_4H_9Cl	25	52	16	58	0	100
iso-$C_5H_{11}Cl$	20	53	24	40	26	36

Note: the tests with iso-C_3H_7Cl were run at 10-12° for 20 hours.

In every case, the decrease in the yield of the monoalkyl benzene was paralleled by an increase in the quantity of the high-boiling condensation products (Table 2). It was found that the higher the molecular weight of the alkyl radical, the more Al was required to secure the individual monoalkyl benzenes.

The condensations of isoamyl and isobutyl chlorides and of the respective bromides involve isomerization. This isomerization is so intensive that the principal reaction products are tertiary butyl- and amylbenzenes:

$$C_6H_6 + (CH_3)_2CHCH_2X \rightarrow C_6H_5C(CH_3)_3$$

$$C_6H_6 + (CH_3)_2CHCH_2CH_2X \rightarrow C_6H_5C(C_2H_5)(CH_3)_2.$$

Isomerization is accompanied by cleavage of the molecules, as was observed in the case of isoamylbenzene, where we discovered a considerable quantity of isopentane. It is likely that this also occurs with isopropyl- and butylbenzenes. Cracking of the side chains may be the probable reason for the decrease in the yield of the higher alkyl benzenes. We may suppose that the process is twofold, as follows:

$$RCl + AlCl_3 \rightarrow R^+AlCl_4^-$$

1. $R^+AlCl_4^- + C_6H_6 \rightarrow C_6H_5R + H^+AlCl_4^-$
2. $R^+AlCl_4^- + H_2 \rightarrow HR + H^+AlCl_4^-$

which explains the formation of alkyl benzenes as well as paraffins. The decrease in the rate of formation of the polyalkyl benzenes in these condensations becomes particularly apparent when we compare the results obtained. In the case of

methyl iodide methylated benzenes are formed, including fairly high yields of penta- and hexamethylbenzenes, whereas isopropyl-, isobutyl-, and isoamyl chlorides and bromides yield only the respective monoalkyl benzenes with traces of di- and trialkyl benzenes.

We condensed benzene with chloroform to determine the feasibility of using polyhalogen derivatives in the Radsiwanowski reaction. The latter author did not secure triphenylmethane when he condensed benzene with chloroform. Friedel and Crafts carried out this reaction, using ordinary $AlCl_3$, but in addition to the triphenylmethane, they secured considerable quantities of diphenylmethane and a black tar that did not distil. They considered the following reactions to have been possible:

$$CHCl_3 + 2C_6H_6 \rightarrow C_6H_5CHClC_6H_5 + 2HCl,$$

$$C_6H_5CHClC_6H_5 + H_2 \rightarrow C_6H_5CH_2C_6H_5 + HCl.$$

They were unable to prove the presence of diphenylchloromethane, however, so that they put forward a no less arbitrary explanation: that the $AlCl_3$ caused the cleavage of the triphenylmethane. The formation of diphenylmethane during this condensation remains a puzzle. Condensations effected by us under various conditions have shown that diphenylmethane is always the principal reaction product of a Radsiwanowski condensation of chloroform and benzene, its yield rising regularly as the percentage of Al in the system is increased:

% Al	2	4	8	20
% Yield $(C_6H_5)_2CH_2$ . .	12	20	29	40

The simplicity of this reaction justifies its recommendation for the preparative production of diphenylmethane. Vacuum distillation of the tar left after the diphenylmethane had been collected yielded a fraction with a b.p. of 190-200° (10 mm), from which we secured pure triphenylmethane (m.p. 91-92°), the yield being only 3-4% of the theoretical, however.

EXPERIMENTAL

Preparation of Radsiwanowski $AlCl_3$. 144% of aluminum shavings (based on the weight of benzene) was added to a flask containing anhydrous benzene, and anhydrous HCl gas was passed through for 3-4 hours at ordinary temperature. The formation of $AlCl_3$ was accompanied by the evolution of bubbles of gas, the benzene grew dark, and the shavings were covered with a deposit of aluminum chloride. After standing overnight, the mixture was ready for the addition of other reaction components.

1. Condensation of benzene with methyl iodide. We explored: the effect of temperature, of the (benzene/methyl iodide) molar proportions, and of the amount of aluminum upon the reaction. We found that the reaction does not take place at 10-12°, so that all subsequent condensations were effected at 40°. After all the methyl iodide had been added, the mixture was heated to 60° for another 3 hours and then decomposed with water. Increasing the amount of catalyst used or increasing the C_6H_6/CH_3I ratio promoted more thoroughgoing condensation: our results indicated that the maximum yields were obtained at 40° with 8% Al and a C_6H_6:CH_3I ratio of 1:3. The condensates were then distilled. The oil with a b.p. in excess of 100°, left behind after driving off the unreacted C_6H_6 and CH_3I, yielded crystals in most instances, which were analyzed separately. The following fractions were collected: 1) 111-113°; 2) 137-144°; 3) 169-176°) 4) 194-205°; and 5) 229-230°. These fractions represent toluene, xylene, and other polymethyl derivatives of benzene, which were not analyzed further. We concentrated upon the crystalline products – penta- and hexamethylbenzenes, which constituted as much as 54% of the fractions with b.p. in excess of 110°. Pentamethylbenzene was recovered from the 210-230° fraction by double fractionation and recrystallization from alcohol. The resulting crystals had a m.p. of 57° (the literature gives the

m.p. as 52-54° and the b.p. as 229°). Hexamethylbenzene was recovered in practically pure state after the methyl iodide and the benzene had been driven off. It had a m.p. of 166-166.5° after recrystallization from alcohol. Hexamethylbenzene is readily soluble in boiling alcohol and in cold benzene and chloroform. It crystallizes from alcohol in the shape of elongated rhombic crystals. The yield was 5-8% of the theoretical.

0.1452 g substance: 0.4966 g CO_2; 0.1579 g H_2O; 0.1232 g substance: 0.3981 g CO_2; 0.1275 g H_2O. 0.1207 g substance: 0.3915 g CO_2; 0.1219 g H_2O. Found %: C 88.24, 88.12, 88.47; H 12.16, 11.58, 11.20; M 159.5, 155.6. $C_{12}H_{18}$. Computed %: C 88.80; H 11.20; M 162.

2. Condensation of benzene with isopropyl chloride and isopropyl bromide. As in all the other instances, the benzene was prepared by distilling commercial benzene, the first 10% of the distillate, which contained water, being discarded. The isopropyl chloride was desiccated above $CaCl_2$ and then distilled. The fraction with a b.p. of 36-36.5° was selected. In determining the effect of the quantity of Al, the tests were run for 20 hours at 10-12°, using 78 g (1 mol) of benzene and 20 g (0.25 mol) of isopropyl chloride. It was found that the yield of isopropylbenzene was a maximum at 2% Al, being 45% of the theoretical. Increasing the percentage of Al still higher promotes the formation of high-boiling products, which total 40% at 8% Al. Varying the C_6H_6/iso-C_3H_7Cl ratio showed that the yield of isopropylbenzene is diminished appreciably by increasing the proportion of the chloride, further condensation then taking place. We obtained the maximum yield of isopropylbenzene (57%) at a C_6H_6/iso-C_3H_7Cl ratio of 1:0.25. With isopropyl bromide the yields did not exceed 31% under the optimum conditions, much more of the high-boiling reaction products being formed in every instance.

We combined the identical fractions of all the tests, as well as the tarry residues with a b.p. of 170°. Repeated fractionation yielded the following fractions: 1) 150-155°; 2) 202-212°; and 3) 233-236°. Fraction (1) was practically pure isopropylbenzene:

d_4^{20} 0.8645; n_D^{18} 1.4681; MR_D 39.85; computed 40.16.

0.1406 g substance: 13.65 g benzene; Δt 0.375°. 0.2330 g substance; 18.00 g benzene: Δt 0.550°. 0.0844 g substance: 0.2776 g CO_2; 0.0756 g H_2O. 0.1134 g substance: 0.3780 g CO_2; 0.1052 g H_2O. Found %: C 89.70, 89.70; H 10.01, 10.48; M 118, 120.1. C_9H_{12}. Computed %: C 90.00; H 10.00; M 120.2.

Fraction (2) was a mixture of meta and ortho diisopropylbenzenes:

d_4^{18} 0.8660; n_D^{18} 1.4880; MR_D 52.29; computed 53.67.

0.2484 g substance: 16.33 g benzene: Δt 0.457°. 0.2492 g substance: 13.18 g benzene: Δt 0.570°. 0.0935 g substance: 0.3035 g CO_2; 0.0945 g H_2O. 0.1020 g substance: 0.3315 g CO_2; 0.1045 g H_2O. Found %: C 88.53, 88.54. H 11.31, 11.46. M 162, 163.4. $C_{12}H_{18}$. Computed %: C 88.89; H 11.11; M 162.1.

The ortho and meta diisopropylbenzenes produced were separated and identified as sulfonamides as follows. 10 ml of the 202-212° fraction was sulfonated with concentrated H_2SO_4. The sulfo acids of ortho and meta diisobutylbenzene were separated by fractional crystallization of their Ba and Cu salts, as outlined by Ulhorn [8]: the barium salt of the sulfo acid of m-diisobutylbenzene is much less soluble in water than the Ba sulfonate of o-diisobutylbenzene, the converse holds true for the Cu salts. We thus isolated the Ba sulfonate of o-diisobutylbenzene and the Cu sulfonate of m-diisobutylbenzene, which were then converted into the sodium salts. The latter were converted into acid chlorides by trituration with PCl_5, the respective sulfamides then being secured by reacting these products with 28% ammonia. Their melting points were as follows after recrystallization from alcohol: 102-103° (Ulhorn gives 102°) for the sulfamide of o-diisobutylbenzenesulfonic acid; and 142-143° (Ulhorn gives 145°) for the sulfamide of m-diiso-

butylbenzenesulfonic acid.

The 233-236° fraction totaled 6.5 g. It was pure triisopropylbenzene:

0.1856 g substance: 19.98 g benzene: Δt 0.240°. 0.1780 g substance: 19.98 g benzene: Δt 0.223°. 0.1221 g substance: 0.3948 g CO_2; 0.1287 g H_2O. 0.0864 g substance: 0.2787 g CO_2; 0.0918 g H_2O. Found %: C 88.11, 87.97; H 11.79, 11.89. M 198.2, 196.5. $C_{15}H_{24}$. Computed: C 88.24; H 11.76; M 204.0.

3. Condensation of benzene with isobutyl chloride and isobutyl bromide. The isobutyl chloride used for this condensation was desiccated above $CaCl_2$; its b.p. was 67-68°. In our study of the effect of the quantity of catalyst used, we ran the tests for 3 hours, boiling a mixture of 78 g (1 mol) of benzene and 23 g (0.25 mol) of isobutyl chloride with 2, 4, and 8% (1.6 g, 3.2 g, and 6.4 g, respectively) of aluminum. No sign of a reaction was observed when the first batches of the chloride were added. The condensation proceeded poorly, probably because of an unfavorable ratio of the reagents, the condensation products totaling only 12-17%. The best yields, as high as 18%, were secured with 2% Al. Any further increase in the amount of Al lowered the yields. Increasing the quantity of isobutyl chloride used increased the yields, to judge by the quantity of the fractions passing over above 85° (2% Al, boiling the mixture for 3 hours):

C_6H_6/iso-C_4H_9Cl	1:0.25	1:0.5	1:1
Fractions with b.p. in excess of 85°	18.65 g	34.9 g	41 g

The yield of the fractions with b.p. above 85° rose to 78.5 g when 1 part of benzene was condensed with 1 part of isobutyl chloride and 4% of Al. The condensates produced in each experiment were suitably treated (decomposing the coordination compounds with water); the oily layer was removed, desiccated with $CaCl_2$, and fractionated. The results of fractionation are listed in Table 3.

TABLE 3

C_6H_6:C_4H_9Cl ratio	Fractions, g					
	65-77°	77-85°	85-165°	165-175°	175-227°	Residue
1:025	–	63.3	1.2	8.4	–	9.0
1:0.5	–	40.7	2.3	17.4	2.7	12.3
1:1(2% Al)	18.1	20.2	5.9	24.0	4.5	6.5
1:1(4% Al)	–	23.0	6.0	34.5	31.5	6.5

Table 3 indicates that the principal product is the 165-175° fraction, which is butylbenzene. The yield of the latter (based on the isobutyl chloride) in per cent of the theoretical) is shown in Table 4.

TABLE 4

C_6H_6:iso-C_4H_9Cl	1:0.25	1:0.5	1:1 (2% Al)	1:1 (4% Al)
$C_6H_5C_4H_9$, (% of the theoretical)	25	26	18	26
Higher boiling products, (% of total quantity of condensation products)	52	45	31	52

Shortening the reaction time from 3 hours to 20 minutes had practically no effect upon the yields. Carrying out the same reaction without the use of heat (at 10-12°) for 18 hours resulted in an increase in the yield of butylbenzene (up to 41% of the theoretical). We ran tests with a C_6H_6:iso-C_4H_9Br ratio of

1:0.25 and 2% Al at various temperatures and reaction times to determine the effect of the nature of the halogen atom upon the condensation. In every case the yields of the fractions with a b.p. in excess of 85° and of the monobutylbenzenes were lower. Identical fractions collected in all the runs were combined and fractionated. The lower fractions constituted unreacted benzene, butyl chloride, and butyl bromide. The major reaction product was the 168-171° fraction, which was monobutylbenzene.

d_4^{18} 0.8690; n_D^{18} 1.4825; MR_D 44.29. Computed 44.48. 0.3088 g substance: 16.30 g benzene: Δt 0.710°; 0.2150 g substance; 16.35 g benzene: Δt 0.5188°; 0.0381 g substance: 0.1248 g CO_2; 0.0361 g H_2O. 0.1260 g substance: 0.4132 g CO_2; 0.1222 g H_2O. Found %: C 89.36, 89.65; H 10.60, 10.85. M 134.2, 130. $C_{10}H_{14}$. Computed %: C 89.55; H 10.45; M 134.1.

The 168-171° fraction may contain the isomeric tert-butylbenzene in addition to isobutylbenzene. The Schramm method [5] was used to separate the former; it is based upon the fact that tert-butylbenzene is insensitive to bromine in direct sunlight, while isobutylbenzene reacts readily, the bromine replacing the hydrogen attached to the tertiary carbon atom. 1.02 g of bromine was gradually added, with agitation, to 19 g of the 168-171° fraction until the color of the mixture remained yellow, after which the mixture was distilled. The bromide was driven off, after which the tert-butylbenzene had a b.p. of 167.5-168.5°. It was identified by synthesizing 2,4-dinitro-1-tert-butylbenzene by heating it for 3 hours to 56-60° with a nitrating mixture. The resultant crystals melted at 60-62° (the m.p. is given as 61-62° in [5]).

Fractionation of the condensates likewise yielded a 220-250° fraction, from which crystals settled out upon standing. These crystals had a m.p. of 75.5-76° after recrystallization from alcohol, which corresponds to the m.p. of 1,4-di-tert-butylbenzene:

0.1280 g substance; 18 g benzene: Δt 0.196°. 0.0888 g substance: 0.2681 g CO_2; 0.0956 g H_2O. 0.0989 g substance: 0.3208 g CO_2; 0.1030 g H_2O. Found %: C 88.18, 88.46; H 12.04, 11.65; M 186. $C_{14}H_{22}$. Computed %: C 88.42; H 11.58; M 190.2.

Distillation of the tarry products yielded a fraction with a b.p. of 300-305°, from which crystals settled out upon standing. The latter had a m.p. of 126-127.5° after recrystallization from alcohol. This is the m.p. of tri-tert-butylbenzene, but we made no further determinations of this substance because of the small quantity available for analysis.

4. Condensation of benzene with isoamyl chloride and isoamyl bromide. The initial isoamyl chloride had a b.p. of 99-101°. We tested the effect of the quantity of Al upon the depth of condensation and the yields of amylbenzene. We used a 1:0.25 ratio of benzene to isoamyl chloride, boiling the mixture for 3 hours. Raising the percentage of Al from 2% to 8% demonstrated that the yield of the 185-191° fraction, representing amyl benzene, increased, even though the aggregate yield of products with boiling points above 85° diminished as the percentage of Al was raised, reaching a maximum of 18.6 g (18%) at 2% Al. Increasing the percentage of isoamyl chloride raised the yield of the condensation products.

C_6H_6:iso-$C_5H_{11}Cl$ ratio	1:0.25	1:0.5
Fractions with b.p. above 85°	18%	52%

The yields of the fractions with boiling points above 85° were about the same, (50 and 52%, respectively) when 2% and 4% Al were employed, the C_6H_6:isoamyl chloride ratio being 1.0:0.5. We ran tests with benzene and isoamyl bromide under the same conditions and using the same proportions in order to determine the effect of

of the nature of the halogen atom upon condensation. The yields of the fractions with boiling points above 85° were somewhat lower. Identical fractions collected in the various fractionations were combined and refractionated. The fraction with a b.p. below 85° yielded isopentane with a b.p. of 29-30°. Neither bromine water nor a permanganate solution reacted with the hydrocarbon.

d_4^7 0.6340; n_D^7 1.36208; MR_D 25.23; computed MR_D 25.17. 0.1154 g substance; 19.98 g benzene: Δt 0.408°. 0.1440 g substance; 19.98 g benzene: Δt = 0.512°. Found: M 72.4, 72.1. C_5H_{12}. Computed: M 72.1.

Amylbenzene, with a b.p. of 188-191°, constituted the bulk of the reaction product; this was proved analytically:

d_4^{18} 0.8710; n_D^{18} 1.48769; MR_D 48.91; computed, 49.07.

0.2168 g substance; 19.53 g benzene: Δt 0.386°. 0.1684 g substance; 19.53 g benzene: Δt 0.303°. 0.1381 g substance: 0.4490 g CO_2; 0.1330 g H_2O. 0.1050 g substance: 0.3440 g CO_2; 0.1040 g H_2O. Found %: C 88.67, 89.35; H 10.77, 11.08; M 147.8, 146. $C_{11}H_{18}$. Computed %: C 88.19; H 10.81; M 148.1.

To judge from its boiling point, the resultant product was chiefly tert-amylbenzene. This was proved by brominating in direct sunlight: 20 g of the amylbenzene absorbed 2.3 g of bromine (bromination of the resultant $C_6H_5CH_2CH_2CH(CH_3)_2$). After the bromine had been removed with alkali, the tert-amylbenzene had a b.p. of 188-190°, which is in agreement with the figure given in the literature.* The 255-270° fraction probably consisted of diisoamyl- or di-terty-amylbenzene, but there was so little of it that all we could do was to determine its molecular weight:

0.1618 g substance; 19.98 g benzene: Δt 0.202°. Found M 205.
$C_{16}H_{26}$. Computed M 218.

The 330-350° fraction yielded a minute quantity of crystals with a m.p. of 151-160° after recrystallization from alcohol (they were not analyzed further).

5. Condensation of benzene with chloroform. In carrying out this portion of the investigation, we wanted to check Radsiwanowski's conclusion that the condensation of benzene with chloroform does not yield triphenylmethane. Numerous experiments under various conditions always yielded a tarry liquid that boiled intermittently and clogged the outlet tubes. Use of a distilling flask with a sabre-shaped tube enabled us to overcome this difficulty, however. The distillate was light-yellow and yielded a considerable quantity of diphenylmethane. Tests showed that the formation of the latter was increased appreciably by raising the per cent of Al used in the reaction:

Per cent Al	4%	8%	20%
Diphenylmethane yield	20%	29%	39%

The yield of diphenylmethane is likewise increased by adding 40% cuprous chloride (this raises the yield of diphenylmethane to 40%). The diphenylmethane fused at 26-27° and boiled at 260-261° (760 mm) and 137° (17 mm), after recrystallization from alcohol. The crystals displayed the characteristic bitter-orange odor of diphenylmethane. The molecular weight was found to be 174 (calculated value: 168.2).

No more than 3-4% of the theoretical quantity of triphenylmethane was recovered from the tarry residue. Triple recrystallization from alcohol of the 196-200° (10 mm) fraction yielded crystals with a m.p. of 91-92° (the m.p. of triphenylmethane is given as 92-93° in the literature). The triphenylmethane was identified by its melting point, its molecular weight, and by analysis.

*The high-boiling products - a small quantity of thick, nearly solid, tar - were not analyzed further.

0.1326 g substance: 0.4528 g CO_2; 0.0808 g H_2O. Found %: C 93.13; H 6.82. $C_{19}H_{16}$. Computed %: C 94.40; H 6.60.

SUMMARY

1. The condensation of halogen alkyl derivatives with benzene and $AlCl_3$–R is performed readily with slight heating for a few hours. The amount of Al required for the condensations is merely 2–4% of the weight of the benzene.

2. The yield of monoalkyl benzenes diminishes as we pass from CH_3I, iso-C_3H_7Cl, and iso-C_4H_9Cl to iso-$C_5H_{11}Cl$. In every case the respective bromides yield somewhat lower yields of the monoalkyl benzenes (some 2–8% less).

3. The condensation of CH_3I with C_6H_6 yields an appreciable quantity of penta- and hexamethylbenzenes (the latter totaling as much as 11.5%). With the other halogen alkyls, the yields of di- and trialkyl benzenes drops sharply as the molecular weight of the radical rises.

4. The condensation of iso-C_4H_9Cl and iso-$C_5H_{11}Cl$ is accompanied by isomerization. The principal products are tert-butyl- and tert-amylbenzenes.

5. In addition to isomerization, the side chain undergoes cracking. The formation of amyl benzenes involves the splitting out of isopentane.

6. The condensation of C_6H_6 with $CHCl_3$ yields up to 38% of diphenylmethane and only 3–4% of triphenylmethane.

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THE BROMINATION OF TERTIARY ALCOHOLS*

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Several investigations have been made of the action of elementary bromine upon tertiary alcohols [1-4]. Still this reaction has remained obscure up to the present time, the interpretations of its mechanism being contradictory. There are two totally different outlines of this reaction given in the literature.

Hell and Urech [4] reacted bromine with 2-methylproponal-2 in carbon disulfide and established qualitatively that sulfuric acid was formed, on this basis alone assuming the reaction to be as follows:

$$(CH_3)_3COH + Br_2 \longrightarrow (CH_3)_3CBr + HBr + O.$$

They did not investigate any other reaction products.

The other equation was based upon a careful investigation of the end products of the bromination of 2-methylpropanol-2, 2-methylpentanol-2, and 2-ethylpentanol-2. It was found that in every case the reaction products were a dibromide and water, and the authors therefore concluded that the reaction takes place in two stages:

$$(R)_2COH-CH_2-R + Br_2 \longrightarrow (R)_2COH-CHBr-R + HBr \rightarrow (R)_2CBr-CHBr-R + H_2O.$$

The first equation, which has established itself in the classical textbooks of organic chemistry [5,6], must doubtless be discarded as obviously incorrect, for it improbably attributes oxidative properties to the alcohol. We believe that the second set of equations is more nearly correct, though it, too, lacks proof, since the partially brominated alcohol – the product of the first stage of the reaction – has not been isolated.

The objective of the present research is determining the equations involved in the reaction of bromine with tertiary alcohols and studying the effect of radicals adjacent to the tertiary alcohol group upon this reaction. We did this by brominating the aliphatic alcohols 2-methylpropanol-2, 2-methylbutanol-2, 2-methylpentanol-2, 3-methylpentanol-3, and 2-methylhexanol-2, and the aliphatic-aromatic alcohols 2-phenylbutanol-2 and 1,1-diphenylpropanol-1. We were also interested in learning the influence of the medium upon the mechanism of this reaction. We did this by brominating the alcohols directly, brominating them in anhydrous carbon disulfide with anhydrous bromine, and brominating them in 80% acetic acid.

The bromine was added a drop at a time to the aliphatic alcohols, as it entered into reaction. The first of these alcohols react slowly with bromine, and heat or activation with direct sunlight is required to speed up the reaction. For instance, rapid bromination of 2-methylbutanol-2 requires heating to 70°, especially at the start of the reaction. The required temperature gradually diminishes as the molecular weight of the alcohol increases, as Henry also noted [7], chilling

*This research was completed in 1941 but the data were lost during the recent war; it is now printed after restoration of much of the material involved.

**Deceased.

being required for the bromination of 3-methylpentanol-3, for the reaction is too violent under ordinary conditions. In every case the reaction mass is a transparent homogeneous mass at the beginning of the reaction, becoming cloudy after about half the calculated quantity of bromine has been added, owing to the water evolved during the reaction. According to the literature [8], the water evolved in the reaction activates the latter considerably, the decolorization of the bromine occurring many times as fast after turbidity sets in. Dibromides were the end products in every experiment in which aliphatic alcohols were brominated directly. We did not find any intermediate reaction product – partially brominated alcohol – under the specified conditions.

The tertiary aliphatic-aromatic alcohols – 2-phenylbutanol-2 and 1,1-diphenylpropanol-1 – were brominated in carbon tetrachloride or chloroform. The principal effect of the aromatic radicals was to make the bromine react extremely vigorously with these alcohols, chilling being required at the very start of the reaction. Moreover, hydrogen bromide was evolved during the addition of the bromine and thereafter. As in the experiments with aliphatic alcohols, the liquid grew turbid after half the bromine had been added, owing to the evolution of water. The end products of the reaction were unsaturated bromides. 2-Phenylbutanol-2 yielded 2-phenyl-3-bromobutene-2, $C_6H_5C(CH_3)=CBr-CH_3$, while 1,1-diphenylpropanol-1 yielded 1,1-diphenyl-2-bromopropene-1, $(C_6H_5)_2C=CBr-CH_3$. Both of these compounds have been prepared previously [9] by reacting bromine with the following hydrocarbons: 2-phenylbutene-2 and 1,1-diphenylpropene-1.

These examples demonstrate the undoubted effect of the radicals attached to the oxidized carbon atom of the alcohol upon the reaction. Though the phenyl radical does not change the course of the reaction, its electronegative nature, apparently, makes it impossible for the bromine atom to stay at the tertiary carbon atom, it splitting off together with the hydrogen attached to the adjacent, less hydrogenated, carbon atom as hydrogen bromide.

As we have said, water is evolved in the bromination of all the alcohols; no doubt this also occurred in Hell's and Urech's experiments. As we know [10], the presence of water and bromine together results in the formation of hypobromous acid, which was oxidized in their experiments to sulfuric acid by the carbon disulfide. To confirm our supposition, we brominated 2-methylpropanol-2 (which had also been brominated by Hell and Urech), 2-methylbutanol-2, 2-methylhexanol-2, 2-phenylbutanol-2, and 1,1-diphenylpropanol-1 in anhydrous carbon disulfide with anhydrous, redistilled bromine. The dibromides described above were secured as the reaction products of all the aliphatic alcohols, unsaturated monobromides being secured from the aliphatic-aromatic alcohols.* Furthermore, it was found that the formation of sulfuric acid is directly related to the rate at which the bromine enters into the reaction. We observed the formation of considerable quantities of sulfuric acid in our experiments with the lower members of the aliphatic alcohols, which are brominated very slowly under ordinary conditions, so that the bromine is in contact with water for a long time, this being a condition that favors the formation of large quantities of hypobromous acid and the latter's oxidizing action on the carbon disulfide. Whenever the bromine was decolorized instantaneously, we found either no sulfuric acid at all or merely traces of it. Thus our results convincingly refute the first reaction equation.

To confirm the second set of equations we had to find conditions that would arrest the reaction at its first stage, the product of which is the partially brominated alcohol. As we know, substitution of a halogen for the alcohol's hydroxyl group occurs when anhydrous hydrohalides or thier concentrated solutions act upon alcohols in the presence of dehydrating agents [11]. Hence, by choosing a suitable solvent for diluting the hydrogen bromide evolved in the reaction, we might expect at least a weakened reaction, if not the complete absence of a reaction

*Water was an unfailing reaction product in the bromination of all the alcohols.

with the partially brominated alcohol – the supposed product of the first reaction stage. The best solvent for this purpose proved to be an 80% aqueous solution of acetic acid. When brominated in 80% acetic acid, all the alcohols, with the sole exception of 1,1-diphenylpropanol-1, yielded unstable compounds that we were unable to isolate, as they decomposed even in vacuum, forming unsaturated bromides and water. The presence of a hydroxyl group and a halogen in the bromination products was established qualitatively, however. When 1,1-diphenylpropanol-1 was reacted with bromine in this solvent, the halogen entered into reaction with great difficulty, heating to 75° being required. No hydrogen bromide was recovered from the reaction mixture. The reaction product proved to be 1,1-diphenyl-2-bromopropanol-1, $(C_6H_5)_2COH-CHBr-CH_3$, the yield being as high as 80%. This is a completely stable substance under ordinary conditions.

Thus, we have established all the stages of the bromination of tertiary alcohols. Our data support the second set of equations, supplementing it – for the aliphatic-aromatic alcohols – by pointing out the transition from a dibromide to an unsaturated bromide, $(R)_2C{=}CBr{-}R$.

EXPERIMENTAL

I. The Bromination of Aliphatic Tertiary Alcohols

1. Action of bromine on 2-methylbutanol-2. The alcohol was prepared from methylmagnesium bromide and acetone; its boiling point was 101-102°. 99 g of bromine was added drop by drop to 54 g of the alcohol. The reaction was extremely slow; the mixture had to be heated to 70° to obtain faster decolorization of the bromine. After half the theoretically required amount of bromine had been added, the whole mixture grew turbid all at once; after that happened, the bromine was decolorized much more rapidly. There were two layers in the reaction mixture – the upper one, of negligible size, consisting of water, and the lower one consisting of the bromide. The reaction products were washed with water, then with a 10% soda solution, and again with water. The bottom layer was removed, desiccated above $CaCl_2$, and distilled at 56-58° and 12 mm. The yield was 75-80° of 2-methyl-2,3-dibromobutane, which is well-known in the literature [12]; d_4^{20} 1.6717; n_D^{20} 1.5112; MR_D 41.47; computed 40.82.

2. Action of bromine on 2-methylpentanol-2. The alcohol was prepared with propylmagnesium bromide and acetone; its boiling point was 121-122°. 95 g of bromine was added dropwise to 60 g of the alcohol. The mixture had to be heated to 65° for the reaction to set in. Otherwise, the procedure was entirely the same as for 2-methylbutanol-2. The reaction product, 2-methyl-2,3-dibromopentane (known in the literature [13]), distilled at 75-78° and 12 mm. The yield was 60-65%. d_4^{20} 1.5634; n_D^{20} 1.4974; MR_D 45.69; computed 45.44.

3. Action of bromine on 3-methylpentanol-3. The alcohol was prepared with ethylmagnesium bromide and methyl ethyl ketone. Its boiling point was 121-122.5° 91 g of bromine was added to 58 g of the alcohol. The reaction set in without heating and was very rapid, otherwise resembling the reactions with the preceding alcohols. The reaction product, 3-methyl-2,3-dibromopentane (mentioned in the literature [14]), had a b.p. of 78-80° at 14 mm. The yield was 60%: d_4^{20} 1.5711; n_D^{20} 1.5005; MR_D 45.64; computed 45.44.

4. Action of bromine upon 2-methylhexanol-2. The alcohol was prepared with butylmagnesium bromide and acetone; it boiled at 141.5-142.5°, with partial decomposition to the hydrocarbon. 76 g of bromine was added to 55 g of the alcohol. The mixture had to be heated to 30° for the reaction to start, but as soon as turbidity set in, the reaction was so violent that the flask had to be chilled. The resulting 2-methyl-2,3-dibromohexane was distilled at 16 mm and boiled at 87-89°. The yield was 55%. It is mentioned in the literature [15]. d_4^{20} 1.4929; n_4^{20} 1.4998; MR_D 50.79; computed 50.06.

II. The Bromination of Aliphatic-Aromatic Tertiary Alcohols

1. Action of bromine on 2-phenylpropanol-2. The alcohol was prepared by a Grignard reaction, with ethylmagnesium bromide and acetophenone; its boiling point was 101-103° at 14 mm. It is an unstable substance, decomposing into water and 2-phenylbutene-2 when distilled at ordinary pressure. It was brominated in carbon tetrachloride and chloroform, 160 g of bromine being added to 150 g of the alcohol. The reaction set in at once, evolving considerable heat, so that chilling with cold water had to be employed while the bromine was added. After half the bromine had been added, the reaction mass grew turbid instantaneously, as in the tests with the aliphatic alcohols, and the reaction rate rose still higher. The water evolved in the reaction collected in a thin layer on the surface of the mixture. In contrast to the bromination of the aliphatic alcohols, the reaction entailed the copious evolution of hydrogen bromide. The reaction products were washed with water, soda, and water again. HBr continued to evolve while the product was being desiccated above $CaCl_2$. After the solvent had been driven off, the residue, totaling 217 g, was distilled three times at 11 mm. The distillation results may be expressed as follows: Fraction I, b.p. 55-110°, 17 g; Fraction II, b.p. 110-118°, 19 g; Fraction III, b.p. 118-120°, 105 g; Fraction IV, b.p. 120-130°, 14 g; Fraction V, b.p. above 130° – tar, 41 g; total 196 g.

The difference of 217 g is accounted for by the solvent and the hydrogen bromide, a fairly large amount of which was evolved at 130°.

Fraction III is a mobile, darkish liquid that affects the eyes intensely. It is readily oxidized by a 1% permanganate solution and adds bromine, but evolves hydrogen bromide as it does so; d_4^{20} 1.3348; n_D^{20} 1.5811; MR_D 52.66; computed 52.08.

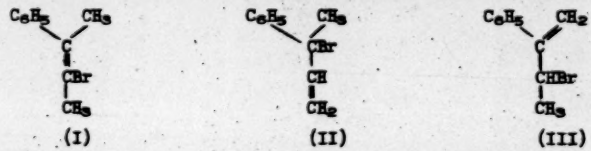
0.1947 g, 0.2134 g substance: 0.1714 g, 0.1899 g AgBr.
Found %: Br 37.46, 37.37. $C_{10}H_{11}Br$. Computed %: Br 37.9.

The substance was oxidized with a 1% permanganate solution to establish the position of the double bond.

Acetophenone was found among the neutral oxidation products; it was identified by its boiling point of 201-202°. Its semicarbazone fused at 194-195°. A eutectic mixture with the semicarbazone of acetophenone exhibited no depression. Analysis of the silver salts of the volatile acids indicated the presence of formic acid (formation of a mirror), plus a copious black precipitate and acetic acid.

Found %: Ag 64.61. $C_2H_3O_2Ag$. Computed %: Ag 64.64.

The monobromide could have been any one of the following three isomers, according to the manner in which the HBr was split out:



(I) (II) (III)

After the volatile acids had been driven off, crystals of benzoic acid settled out of the residue; they were sublimed, after which they fused at 120.5-121°. Their eutectic mixture with benzoic acid exhibited no depression.

Thus, the hydrogen bromide was split out by detaching a halogen atom from the tertiary carbon atom and a hydrogen atom from the adjacent brominated carbon atom, so that the substance has the structural formula I.

2. Action of bromine on 1,1-diphenylpropanol-1. The alcohol was prepared by a Grignard reaction, from ethylmagnesium bromide and benzophenone. Its melting point was 93-93.5°. Bromination was carried out in $CHCl_3$ and CCl_4. The reaction was vigorous from the very beginning, water and HBr being evolved. The reaction product was washed with water, soda, and again water; after it had been desiccated above $CaCl_2$ and the solvent had been driven off, it crystallized. It fused at 48-48.5° after recrystallization from alcohol, [9].

0.2091 g, 0.2231 g substance: 0.1415, 0.1544 g AgBr.
Found %: Br 28.8, 29.37. $C_{15}H_{13}Br$. Computed %: Br 29.28.

III. The Bromination of Tertiary Alcohols Under Anhydrous Conditions in Carbon Disulfide

The alcohols and the carbon disulfide were carefully desiccated. The bromine was desiccated and distilled with $CaBr_2$. These were the conditions used in brominating 2-methylpropanol-2, which Hell and Urech had brominated, 2-methylbutanol-2, 3-methylpentanol-3, 2-methylhexanol-2, 2-phenylbutanol-2, and 1,1-diphenylpropanol-1. The bromine reacted extremely slowly with the first two alcohols, the reaction mixture's turbidity, due to the evolution of water, becoming apparent only after 2 to 3 days had elapsed. A test with barium chloride yielded a copious precipitate of barium sulfate. The reaction was much faster with 3-methylpentanol-3, only a slight amount of precipitate being thrown down when a $BaCl_2$ solution was added. No barium sulfate precipitate was observed at all when 2-phenylbutanol-2 and 1,1-diphenylpropanol-1 were brominated, the bromine reacting with these two instantaneously. The reaction products were dibromides for the aliphatic alcohols and unsaturated monobromides for the aliphatic-aromatic alcohols.

IV. The Bromination of 1,1-Diphenylpropanol-1 in 80% Acetic Acid

10 g of the alcohol was dissolved by heating it gently in 80% acetic acid. Then 11 g of bromine was slowly added, drop by drop, at the rate at which it entered into reaction, it being quickly decolorized when the reaction mixture was heated to 60-65°. No hydrogen bromide was evolved. After the reaction was over, the mixture was diluted with water, and the acetic acid was gradually neutralized with soda; this caused a thick yellowish oil to settle out, which floated upward and crystallized when the solution was saturated with soda. The crystals were collected, and the aqueous layer was twice extracted with ether. The ether extract was washed with water, and then the crystals were dissolved in it. The solution was desiccated, filtered, and set aside to crystallize. The next day large crystals were found, which melted at 56.5-57°. The yield was 11 g, or 80% of the theoretical. The substance is readily soluble in ether, chloroform, benzene, acetone, and acetic acid, but less so in ethyl alcohol, from which it was recrystallized. It fused at 57° after recrystallization. It does not decolorize permanganate in acetone solution; it indicates the presence of a halogen and active hydrogen.

0.1974 g substance: 0.1264 g AgBr; 0.2119, 0.0920 g substance: 16.4, 7.5 ml CH_4 (0°, 760 mm). Found %: Br 27.25; Oh 5.91, 6.23. $C_{15}H_{15}OBr$. Computed %: Br 27.48; OH 5.8; 0.0838 g substance: 17.796 g benzene: Δt 0.089°: Found: M 288.1. Computed: M 290.92.

SUMMARY

1. 2-Methylbutanol-2, 2-methylpentanol-2, 3-methylpentanol-3, 2-methylhexanol-2-, 2-phenylbutanol-2, and 1,1-diphenylpropanol-1 have been brominated.

2. All the stages of the reaction involved in the bromination of tertiary alcohols have been determined.

3. It has been shown that the equations for the bromination of tertiary alcohols proposed by Hell and Urech are incorrect and that bromination in carbon disulfide cannot serve as a qualitative reaction for a tertiary alcohol group.

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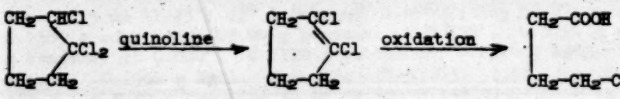
RESEARCHES ON UNSATURATED CYCLIC HYDROCARBONS AND THEIR HALOGEN DERIVATIVES

X. TRANSFORMATIONS OF SATURATED AND UNSATURATED HALOGEN DERIVATIVES OF CYCLOPENTANE

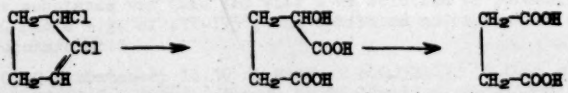
N. A. Domnin and L. I. Ikhova

One of the present authors has discovered interesting transformation of 1,2-dichlorocyclohexene-2 when it is acted upon by zinc dust and metallic sodium. These transformations enabled him to draw several stereochemical inferences regarding the trend of reactions in which halogen atoms are detached from halogen derivatives of cyclic hydrocarbons [1]. As we know, five- and six-membered rings have different structures, and we were therefore interested in learning the similarities and differences between these two cyclic systems with respect to the transformations that had already been explored for a six-membered ring [1].

The action of molecular chlorine upon 1-chlorocyclopentene-1 (I) in a D.V. Tishchenko reaction [2] yielded a mixture of products, consisting of 1,1,2-trichlorocyclopentane (II) (22%) and 1,2-dichlorocyclopentene-2 (IV) (44%). The action of quinoline on 1,1,2-trichlorocyclopentane (II) yields 1,2-dichlorocyclopentene-1 almost quantitatively, oxidation of the latter yielding glutaric acid:



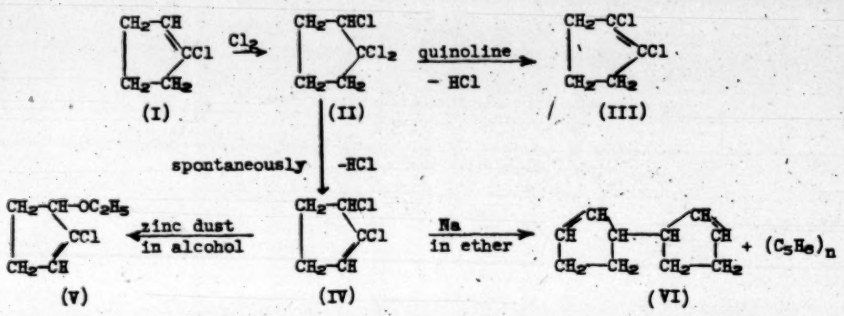
Oxidation of 1,2-dichlorocyclopentene-2 with a 2% solution of permanganate yields succinic acid as follows:



The reaction of 1,2-dichlorocyclopentene-2 with zinc dust in alcoholic solution yields 2-chloro-1-ethoxycyclopentene-2 (V). Reacting 1,2-dichlorocyclopentene-2 with metallic sodium in an ether solution yields a dimeric product (VI) plus polymeric products.

This research may be represented by the following diagram: (see following page).

Thus, all the transformations of halogen derivatives of cyclopentane follow the same pattern as that of the analogous halogen derivatives of cyclohexane [1]



Thus, all the transformations of halogen derivatives of cyclopentane follow the same pattern as that of the analogous halogen derivatives of cyclohexane [1].

EXPERIMENTAL

Cyclopentanone was prepared from adipic acid by the Boedtker method [3], reacting it with phosphorus pentachloride to yield a mixture of the dichloride and the unsaturated monochloride. Reacting quinoline with this mixture yielded 1-chlorocyclopentene-1:

b.p. 112-114°: d_4^{20} 1.044; MR_α 27.25; computed 27.32.

1-Chlorocyclopentene-1 was chlorinated with molecular chlorine by the D.V. Tishchenko method [2], the reaction product being fractionated. Repeated fractionations into a column yielded two fractions with b.p. of 41-43° and 57-59° at 5 mm. Analysis indicated that the substance in Fraction I was 1,2-dichlorocyclopentene-2, and that in Fraction 2 was 1,1,2-trichlorocyclopentane.

1,2-Dichlorocyclopentene-2:

B.p. at 5 mm 41-43°; d_4^{20} 1.244; n_α^{20} 1.49602; MR_D 32.27; computed 32.16. 0.3383 g substance; 23.94 g benzene: Δt 0.525°. 0.5796 g substance; 23.94 g benzene: Δt 0.880°. 0.1110 g substance: 0.2316 g AgCl. 0.1421 g substance. 0.2962 g AgCl. Found %: Cl 51.63, 51.58, (Carius); M 138.3, 140.3. $C_5H_6Cl_2$. Computed %: Cl 51.82; M 137.01.

The substance was oxidized with a 2% solution of permanganate. The resulting acid had a m.p. of 172-173°, and exhibited no depression when mixed with known succinic acid.

0.0552 g substance; 11.30 ml NaOH (T 0.003216). 0.0696 g substance; 14.60 ml NaOH (T 0.003216). Found: neutralization equivalent 60.70, 60.58. Computed: 59.05.

Analysis of the silver salts: 0.1223 g substance: 0.0792 g Ag. 0.1018 g substance: 0.0660 g Ag. Found %: Ag 64.76, 64.85. $C_4H_4O_4Ag_2$. computed %: Ag 65.05.

1,1,2-Trichlorocyclopentene

B.p. at 5 mm 57-59°; d_4^{20} 1.356; n_α^{20} 1.49744; MR_α 37.35. Computed 37.50. 0.1533 g substance; 23.93 g benzene: Δt 0.205°. 0.2811 g substance; 23.93 g benzene: Δt 0.370°. 0.1625 g substance: 0.4008 g AgCl. 0.1437 g substance: 0.3536 g AgCl. Found %: Cl 61.03, 60.92 (Carius); M 164.0, 163.3. $C_5H_7Cl_3$. Computed %: Cl 61.32; M 173.5.

1,2-Dichlorocyclopentene-1. 20 g of 1,1,2-trichlorocyclopentane was gradually added from a dropping funnel to 22.3 g of quinoline heated to 130° in a flask. A 145-155° distillate was collected, washed, and desiccated. Fractionation of the distillate at 5 mm yielded 6 g of a substance, almost all of which distilled over at 38-39° in a second fractionation.

d_4^{20} 1.252; n_α^{20} 1.49369; MR_α 31.91; computed 32.16.

0.1196 g substance; 19.21 g benzene: Δt 0.230°. 0.2066 g substance; 19.21 g benzene: Δt 0.410°. 0.1176 g substance: 0.3459 g AgCl. 0.1636 g substance: 0.4070 g AgCl. Found %: Cl 51.68, 51.60 (Carius): M 139.1, 134.9. $C_5H_8Cl_2$. Computed %: Cl 51.82; M 137.0

When 1,2-dichlorocyclopentene-1 was oxidized with a 2% permanganate solution, we got an acid with a m.p. of 193°. A test sample, mixed with known glutaric acid, exhibited no depression.

0.0991 g substance: 13.95 ml NaOH (T 0.004292). 0.0488 g substance: 6.80 ml NaOH (T 0.004292). Found: neutralization equivalent 66.30, 67.10. $C_5H_8O_4$. Computed: 66.05.
Analysis of the silver salts: 0.1266 g substance: 0.0783 g Ag. 0.1096 g substance: 0.0680 g Ag. Found %: Ag 62.03, 62.09. $C_5H_6O_4Ag_2$. Comp. % Ag 62.40.

Action of zinc dust on 1,2-dichlorocyclopentene-2. 47 g of zinc dust and 50 ml of 96% ethyl alcohol were placed in a flask fitted with a reflux condenser. As the flask was heated over a water bath until the alcohol boiled, 20 g of 1,2-dichlorocyclopentene-2 was added to it from a dropping funnel, after which the flask was heated for another 27 hours. The reaction was carried out in a current of carbon dioxide. The liquid was then separated from the precipitate by filtration and diluted with water, which caused the liquid to separate into two layers. The bottom layer was separated from the upper aqueous layer, diluted with ether, and desiccated; after the ether had been driven off, it was fractionated.

This yielded 6 g of a substance at 64-65° and 6 mm, which was then analyzed.

2-Chloro-1-ethoxycyclopentene-2:

B.p. 64-65° at 16 mm; d_4^{20} 1.0632; n_α^{20} 1.46014; MR_α 37.88; computed 38.16. 0.0815 g substance; 19.57 g benzene: Δt 0.150°. 0.1316 g substance; 19.57 g benzene: Δt 0.245°. 0.2121 g substance: 0.3375 g AgI. Found %: C_2H_5O 30.33 (Zeisel); M 140.0, 143.0. $C_7H_{11}OCl$. Computed %: C_2H_5O 30.71; M 146.5. 0.2279 g substance: 0.2262 g AgCl. 0.0962 g substance: 0.0959 g AgCl. Found %: Cl 24.56, 24.62 (Carius). $C_7H_{11}OCl$. Computed %: Cl 24.23.

The substance is colorless and mobile and has a pleasant odor.

Reaction of metallic sodium with 1,2-dichlorocyclopentene-2. 50 ml of anhydrous ether and 4.5 g of freshly cut metallic sodium were placed in a flask fitted with a reflux condenser and a calcium-chloride tube. After no more hydrogen was evolved from the ether, 17 g of 1,2-dichlorocyclopentene-2 was added to the flask. The reaction lasted two days at ordinary temperature. The liquid in the flask was then separated from the solids, and the ether was driven off. The residue left in the flask was only partially distilled at 13 mm and 65-105°, yielding 2 g of distillate, most of the residue not distilling without decomposition. The 2 g of substance was fractionated at 6 mm, the following fractions being collected: I) 50-56°; and II) 60-80°. Fraction I yielded 0.2 g at 52-54°; Fraction II yielded a few drops at 50-74°.

The amount recovered of Fraction I sufficed only for a determination of the molecular weight.

0.1198 g substance; 19.41 g benzene: Δt 0.24°. Found: M 132.0.
$C_{10}H_{14}$. Computed: M 134.0.

SUMMARY

1. The following compounds have been synthesized and identified for the first time: 1) 1,2-dichlorocyclopentene-2; 2) 1,2-dichlorocyclopentene-1; 3) 1,1,2-trichlorocyclopentane; and 4) 2-chloro-1-ethoxycyclopentene-2.

2. The action of molecular chlorine on 1-chlorocyclopentene-1 yields a mixture of products, consisting of 1,1,2-trichlorocyclopentane (22%) and 1,2-dichlorocyclopentene-2 (44%).

3. The action of quinoline upon 1,1,2-trichlorocyclopentane yields 1,2-dichlorocyclopentene-1 quantitatively.

4. The classic methods of synthesizing allene hydrocarbons with an open chain prove unsuitable for introducing an allene bond into a five-membered ring.

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THE STRUCTURE OF EINHORN'S "2-HYDROXY-5-NITROBENZYLDIETHYLAMINE"

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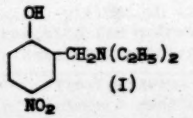
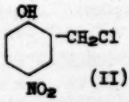
In the course of synthesizing antimalarials we found it necessary to synthesize 2-hydroxy-5-nitrobenzyldiethylamine (I).

In the literature on this subject this compound has been described by Einhorn and his associates [1]; they synthesized this substance from 2-hydroxy-5-nitrobenzyl chloride (II) and diethylamine. The synthesis of the required 2-hydroxy-5-nitrobenzyl chloride is described in the literature [1,2,3]. According to [1,3], the initial material for this latter synthesis was p-nitrophenol, the chloromethylating agent being "chloromethyl alcohol" and zinc chloride or methylal and hydrogen chloride. The authors of paper [2] started with 2-hydroxy-5-nitrobenzyl alcohol and passed hydrogen chloride through an alcoholic solution of the former.



(I)



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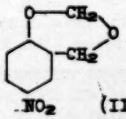

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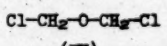

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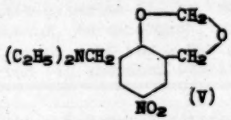

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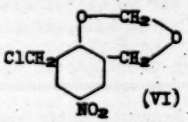


(VI)

In the patent [3] covering the synthesis of 2-hydroxy-5-nitrobenzyl chloride the formation of only this one substance, with a m.p. of 132°, is described. Einhorn and his associates [1] used about three times as much zinc chloride as is called for in the patent and synthesized 2-hydroxy-5-nitrobenzyl chloride with a m.p. of 128° and some 50% of 5-nitrosaligenin methylene ether (III), with a m.p. of 148°.

The end product secured by Einhorn and his associates, and described by them as 2-hydroxy-5-nitrobenzyldiethylamine (I), consisted of light-yellow needles with a m.p. of 68-69° after recrystallization from aqueous alcohol; its hydrochloride consisted of colorless crystals, with a m.p. of 197° with decomposition. The analyses for C, H, and N cited in the Einhorn paper exhibit about 0.5% less nitrogen than the computed values.

Though the results of the analysis of nitrogen in the 2-hydroxy-5-nitrobenzyldiethylamine caused some doubt as to the identity of this product, we synthesized it nevertheless by the method specified above (the Einhorn method), making

a slight change in the chloromethylating agent; our results were unexpected, insofar as the structure of the Einhorn product was concerned.

We synthesized 2-hydroxy-5-nitrobenzyl chloride (II) from p-nitrophenol in the presence of zinc chloride, using dichlorodimethyl ether (IV) instead of chloromethyl alcohol. The solid reaction product was separated into two parts on the basis of their different solubilities in ether. The substance that was freely soluble in ether had a m.p. of 124-126° after several recrystallizations from benzene. The substance that was sparingly soluble fused at 92-93° and had a m.p. of 103.5-104° after being recrystallized from petroleum ether. Treating the substance with a m.p. of 124-126° with diethylamine dissolved in alcohol yielded a bright-yellow product, which consisted of hardly colored, slightly yellow needles, with a m.p. of 68°, after repeated recrystallization from aqueous alcohol; its hydrochloride was white, with a m.p. of 197° with decomposition. We obtained an absolutely identical product by reacting the substance with a m.p. of 103.5-104° with diethylamine, but in contrast to the previous case, the product was secured in the pure state at once. The melting points of the base and of its hydrochloride were the same as those cited for Einhorn's 2-hydroxy-5-nitrobenzyldiethylamine. The properties of the base and the analyses of this product occasioned some doubt, however, regarding the correctness of the structure attributed to this product. The base proved to be insoluble in dilute alkalis, for example, and did not yield the characteristic color with ferric chloride, which seemed to be somewhat unusual for a compound that contained a phenolic hydroxy group. Our analyses for nitrogen indicated as much as 1.5% less nitrogen than what was called for theoretically. Repeated recrystallization of the substance did not improve the nitrogen analysis figure.

Reduction of the nitro product we had secured (with iron in hydrochloric acid) yielded an amino compound that likewise failed to exhibit a satisfactory reaction for a free hydroxy group. Analyses of this amino compound also yielded a smaller percentage of nitrogen than the figure called for.

The foregoing compelled us to undertake an investigation of the structure of Einhorn's substance with a m.p. of 68°, to which the authors had ascribed the structure of 2-hydroxy-5-nitrobenzyldiethylamine (I). We did this by synthesizing 2-hydroxy-5-nitrobenzyldiethylamine (I) by two other methods: a) by the Mannich reaction, from p-nitrophenol, formaldehyde, and diethylamine; and b) by introducing the chloromethyl group into the p-nitrophenol molecule by means of methylal and hydrogen chloride [4] and then substituting the diethylamino group for the chlorine.

The properties of the 2-hydroxy-5-nitrobenzyldiethylamine produced by these methods were compared with those of the product synthesized by Einhorn (cf. the table).

As we see it, the bright-yellow color of 2-hydroxy-5-nitrobenzyldiethylamine and its ready solubility in water are due to the formation of intramolecular or intermolecular salts between the acid hydroxy group and the basic $N(C_2H_5)$ group. This supposition is supported by the existence of a salt of o-nitrophenol and methylamine [5].

Analyses of the base and of the hydrochloride of the 2-hydroxy-5-nitrobenzyldiethylamine we synthesized by the method outlined yielded composition percentages that agreed with the calculated values.

These figures rendered the structure attributed by Einhorn to the product he synthesized and identified as 2-hydroxy-5-nitrobenzyldiethylamine obviously incorrect.

We then made a comprehensive investigation of the Einhorn substance with a

	Einhorn's 2-hydroxy-5-nitrobenzyldiethylamine	2-Hydroxy-5-nitrobenzyldiethylamine synthesized in the present research
Color	Hardly any color, barely yellow	Bright yellow
M.p. of the base	68-69°	87°
M.p. of the hydrochloride	197°	223-224°*
Solubility	Freely soluble in alcohol, ether, benzene, and dilute acids; insoluble in water and dilute alkalies	Freely soluble in alcohol, benzene, water, dilute acids, and dilute alkalies
Crystallization	From aqueous alcohol	From water or benzene
Reaction with ferric chloride	None	Dark-crimson color

m.p. of 68-69° in order to determine its structure. The presence of a nitro group in this compound was proved by its reduction to an amino group, the presence of the latter being established by diazotization, followed by azo coupling and condensation with compounds that contained an active halogen atom. There was no doubt about the introduction of a diethylaminomethyl group during the reaction described by Einhorn for the synthesis of this product, in the light of the mobility of the halogen atom in the initial product and the properties of the substance produced.

No free hydroxy group was found in the Einhorn substance – the product did not dissolve in dilute alkalies nor did it color ferric chloride. We therefore supposed that the hydrogen in the hydroxy group of Einhorn's product was not free, and we proposed to substitute a CH_2OH group for this hydrogen, in line with the nature of the reacting constituents. To establish the presence of this group, Einhorn's product was heated with hydrobromic acid (sp. gr. 1.48) to secure a brominated derivative involving the replacement of the OH group by bromine. We did not find a substance possessing the usual typical properties of a halogen derivative in the products of this reaction, however. Instead, the sharp odor of formaldehyde was noticed when we heated Einhorn's product with hydrobromic acid, and the acid solution yielded a substance whose properties greatly resembled those of the 2-hydroxy-5-nitrobenzyldiethylamine (I) we had synthesized. This resemblance was noticeable in the color, solubility and proximity of the melting point (81-82°). Still, a test sample of the resultant product exhibited a depression of 12-15° when mixed with 2-hydroxy-5-nitrobenzyldiethylamine. Nor did the melting point of the hydrochloride (167°) agree with that of the hydrochloride of 2-hydroxy-5-nitrobenzylidethylamine. The evolution of formaldehyde when the Einhorn product was treated with HBr, together with its other properties, suggested that the Einhorn product with a m.p. of 68-69° is 3-diethylaminomethyl-5-nitrosaligenin methylene ether (V). To prove this we reacted the 5-nitrosaligenin methylene ether (III), synthesized in accordance with [7], with dichlorodimethyl ether and zinc chloride under the same conditions as we had previously employed for p-nitrophenol. This gave an 88% yield of 3-chloromethyl-5-nitrosaligenin methylene ether (VI), with a m.p. of 103-104°.

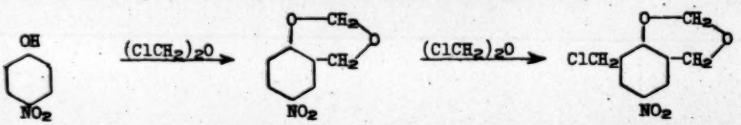
A test sample, mixed with the substance with a m.p. of 103.5-104° that we had secured by reacting dichlorodimethyl ether with p-nitrophenol, exhibited no depression. The resultant 3-chloromethyl-5-nitrosaligenin methylene ether (VI) was treated with diethylamine dissolved in alcohol. This yielded a substance

*In 1948 a paper was published [6] describing the synthesis of 2-hydroxy-5-nitrobenzyldiethylamine by this same method and giving the same melting point for the hydrochloride.

with a m.p. of 68°. Its hydrochloride melted at 197°. A test sample exhibited no depression when mixed with Einhorn's product.

Thus, the product that Einhorn gave the structure of 2-hydroxy-5-nitrobenzyldiethylamine is actually 3-diethylaminomethyl-5-nitrosaligenin methylene ether (V).

We picture the formation of 3-chloromethyl-5-nitrosaligenin methylene ether (VI) when dichlorodimethyl ether is reacted with p-nitrophenol as follows: first the 5-nitrosaligenin methylene ether (III) is formed. The dichlorodimethyl ether then reacts with the 5-nitrosaligenin methylene ether, converting the latter into 3-chloromethyl-5-nitrosaligenin methylene ether (VI):



When reacted with diethylamine, the latter yields 3-diethylaminomethyl-5-nitrosaligenin methylene ether (V), with a structure like that of the Einhorn product.

EXPERIMENTAL

Action of dichlorodimethyl ether on p-nitrophenol. p-Nitrophenol (10 g) and dichlorodimethyl ether (10 g) were placed in a three-necked flask, fitted with a stirrer, a condenser, and a thermometer; 20 g of zinc chloride was then added in small batches with constant stirring. The flask contents were heated to 30° over a water bath, which initiated a vigorous reaction, hydrogen chloride being evolved and the reaction mass foaming up. Everything dissolved, and the solution was then heated for another hour, with constant stirring, the bath temperature being 40°, after which it was set aside overnight. The solid white product was triturated in a mortar with water to eliminate the zinc chloride and was extracted while moist with ether. Driving off the ether left behind 8.5 g of a product with a m.p. of 110-112°. It fused at 124-126° after repeated recrystallization from benzene. Part of the substance (4.8 g), which was more sparingly soluble in ether, was not extracted; m.p. 92-93°. Its m.p. was 103.5-104° after recrystallization from petroleum ether. White needles.

Determination of nitrogen in the substance with a m.p. of 103.5-104°. 6.200 mg substance: 0.333 ml N_2 (19°, 752 mm). 5.397 mg substance: 0.284 ml N_2 (16°, 772 mm). Found %: N 6.31, 6.31.

Action of diethylamine on the substance with a m.p. of 124-126°. The substance with a m.p. of 124-126° (8.5 g), diethylamine (10 ml), and absolute alcohol (50 ml) were heated to the boiling point for 6 hours. The alcohol and the excess diethylamine were driven off, and the residual liquid was dissolved in 10% hydrochloric acid, agitated with charcoal, and filtered. The filtrate was saturated with potash. The bright-yellow oil that settled out soon solidified; total - 7.6 g. After being triply recrystallized from aqueous alcohol, the substance consisted of pale-yellow needles with a m.p. of 67-68°; it totaled 3.6 g. The base is freely soluble in alcohol, ether, and benzene; it is soluble in acids, but is insoluble in water or alkalies.

4.460 mg substance: 0.421 ml N_2 (20°, 728 mm). 4.348 mg substance: 0.421 ml N_2 (20°, 724 mm). Found %: N 10.53, 10.75.

The white hydrochloride crystallizes out of alcohol or 10% hydrochloric acid; its m.p. is 197° with decomposition.

3.278 mg substance: 0.274 ml N_2 (24°, 748 mm). 4.001 mg substance: 0.323 ml N_2 (24°, 756 mm). Found %: N 9.45, 9.24.

2-Hydroxy-5-nitrobenzyldiethylamine was synthesized in two ways: a) from p-nitrophenol, formaldehyde, and diethylamine in the Mannich reaction; and b) from 2-hydroxy-5-nitrobenzyl chloride by reacting the latter with diethylamine.

a) p-Nitrophenol (23.2 g) was placed in a three-necked flask fitted with a reflux condenser, a stirrer, a thermometer, and a dropping funnel, and 13.4 g of diethylamine was added a drop at a time to keep the temperature from rising above 20°. Then 17 g of formalin (38%) was added, gradually diluting the mixture. Stirring was continued for another 15 minutes at room temperature, and for two hours at 80°. The resulting liquid reaction mass was heated to 80° over a water bath in a 13-14 mm vacuum to drive off the unreacted diethylamine and formaldehyde. The remaining 31.2 g of a thick, red oil was treated with a 10% solution of hydrochloric acid. The resultant white hydrochloride was dissolved in 100 ml of water and extracted repeatedly with ether to remove the unreacted p-nitrophenol. The aqueous solution of the hydrochloride was saturated with potash, and the base that settled out was extracted with ether. The ether solution was desiccated with potash. Driving off the ether left behind 15 g of a red liquid which was converted into a hydrochloride by treating the base with alcoholic HCl and adding ether. The hydrochloride was crystallized from 10% hydrochloric acid or from alcohol. Its m.p. was 223-224° with decomposition. The hydrochloride is fairly readily soluble in water, forming a yellowish solution; it is soluble in alcohol and dilute acids, but is insoluble in acetone or ether.

6.556 mg substance: 0.637 ml N_2 (18°, 724 mm). 4.623 mg substance: 0.441 ml N_2 (20°, 742 mm). Found %: N 10.86, 10.85.
$C_{11}H_{17}O_3N_2Cl$. Computed %: N 10.75.

Dissolving the hydrochloride in water and then saturating the solution with potash yielded the base 2-hydroxy-5-nitrobenzyldiethylamine. The base is a bright-yellow solid that is freely soluble in water, alcohol, benzene, and dilute acids and alkalies. It crystallizes out of water in platelets with a m.p. of 87°. It turns a ferric-chloride solution dark crimson.

6.188 mg substance: 0.706 ml N_2 (20°, 726 mm). 4.000 mg substance: 0.461 ml N_2 (20°, 726 mm). Found %: N 12.70, 12.83. $C_{11}H_{16}O_3N_2$. Computed %: N 12.50.

b) 2-hydroxy-5-nitrobenzyl chloride (18 g), diethylamine (30 ml), and absolute alcohol (40 ml) were boiled together for 3 hours over a water bath. The alcohol and the excess diethylamine were driven off, and the remaining thick, red liquid was dissolved in 10% hydrochloric acid, agitated with charcoal, and filtered. The white crystals of the hydrochloride that settled out upon standing were filtered out and dissolved by heating them in 50 ml of water. The solution was clarified with charcoal, filtered, and saturated with potash. The reddish oil that settled out solidified upon cooling and trituration to a bright-yellow product. Total: 8.6 g. The hydrochloride filtrate was neutralized and likewise saturated with potash. The red oil that settled out was extracted with ether, and the ether solution was saturated with potash. Driving off the ether left behind 10.4 g of a thick red oil. The synthesized base totaled 19 g, the yield of crude product being 88.4%.

The base and the hydrochloride were purified by the methods set forth above. The melting point of the base was 87° and that of the hydrochloride 223-224°. A mixed test sample of the bases 2-hydroxy-5-nitrobenzyldiethylamine prepared by methods (a) and (b) exhibited no depression, nor did a mixed test sample of their hydrochlorides.

3-Chloromethyl-5-nitrosaligenin methylene ether (VI). 7.6 g of 5-nitrosaligenin methylene ether [7] and 7.6 g of dichlorodimethyl ether were placed in a three-necked flask fitted with a stirrer, a thermometer, and a condenser (or a glass tube with a drawn-out tip), and 15.2 g of zinc chloride was added a little at a time with constant stirring. The flask was heated over a water bath; the mass softened at a temperature of about 40° and turned liquid between 50 and 60°. Stirring was continued at the latter temperature for an hour. The contents of the flask solidified when they were cooled to 40°; then they were set aside to stand overnight. The resultant white solid was triturated with water in a mortar, filtered out, and washed thoroughly. It totaled 8.6 g, with a m.p. of 101-102°, the yield being 88%. White needles with a m.p. of 103.5-104° after recrystallization from petroleum ether. A test sample exhibited no depression when mixed with the product synthesized by reacting dichlorodimethyl ether with p-nitrobenzene ene, which has a m.p. of 103.5-104°.

3-Chloromethyl-5-nitrosaligenin methylene ether is freely soluble in benzene and alcohol and soluble in petroleum ether; it is insoluble in water, mineral acids, and alkalies. It crystallizes from alcohol, petroleum ether, and heptane.

4.444 mg substance: 0.245 ml N_2 (23°, 744 mm). 5.797 mg substance: 0.314 ml N_2 (22°, 744 mm). 3.607 mg substance: 6.224 mg CO_2; 1.183 mg H_2O. 3.892 mg substance: 6.722 mg CO_2; 1.222 mg H_2O. Found %: N 6.22, 6.14; C 47.09, 47.13; H 3.67, 3.51. $C_9H_8O_4NCl$. Computed %: N 6.10; C 47.06; H 3.48.

3-Diethylaminomethyl-5-nitrosaligenin methylene ether (V). 8 g of 3-chloromethyl-5-nitrosaligen methylene ether, 15 ml of diethylamine, and 50 ml of absolute alcohol were heated over a water bath to the boiling point of the mixture for 6 hours. The alcohol and the excess diethylamine were driven off; the residual reddish liquid was dissolved in 10% hydrochloric acid, agitated with charcoal, filtered, and alkalinized with 10% caustic soda. The slightly yellowish product that settled was filtered out and washed with water. It totaled 6.7 g and had a m.p. of 62-63°. The substance consisted of elongated needles with a m.p. of 68° after recrystallization from alcohol. 3-Diethylaminomethyl-5-nitrosaligenin methylene ether is freely soluble in alcohol, ether, and benzene; it is soluble in acids, but insoluble in water or alkalies. A test sample exhibited no depression when mixed with the Einhorn product, which had a m.p. of 67-68°.

6.498 mg substance: 0.608 ml N_2 (20°, 752 mm). 6.348 mg substance: 0.598 ml N_2 (21°, 751 mm). 3.989 mg substance: 8.609 mg CO_2; 2.485 mg H_2O. 3.839 mg substance: 8.266 mg CO_2; 2.363 mg H_2O. Found %: N 10.78, 10.81; C 58.90, 58.76; H 6.97, 6.89. $C_{13}H_{18}O_4N_2$. Computed %: N 10.53; C 58.65; H 6.77.

The white hydrochloride crystallizes from alcohol or 10% hydrochloric acid; its m.p. was 197°.

6.496 mg substance: 0.529 ml N_2 (21°, 744 mm). 7.132 mg substance: 0.568 ml N_2 (22°, 752 mm). Found %: N 9.26, 9.12. $C_{13}H_{19}O_4N_2Cl$. Computed %: N 9.26.

3-Diethylaminomethyl-5-aminosaligenin methylene ether. 16 g of iron filings and 30 ml of water were placed in a flask fitted with a stirrer, a condenser, and a dropping funnel, and 12 ml of concentrated hydrochloric acid was added to the slightly heated solution a drop at a time. After this was completed, 18 g of 3-diethylaminomethyl-5-nitrosaligenin methylene ether was added to the flask a little at a time. Heating was continued for an hour after the nitro product had been added. After it had cooled, the sludge was filtered out of the liquid, which was then alkalinized with 10% caustic soda. The dark oil that settled out

was extracted with ether; the ether solution was desiccated with potash. The thick, reddish oil left after the ether had been driven off distilled in a 2-2.5 mm vacuum at 175-176°. The distillate totaled 10.7 g, or a yield of 67%. The base was a viscous liquid, freely soluble in ether and benzene, soluble in acids, and insoluble in water and alkalies.

4.300 mg substance: 0.441 ml N_2 (20°, 767 mm). 5.444 mg substance: 0.549 ml N_2 (20°, 767 mm). Found %: N 12.06, 11.86. $C_{13}H_{20}O_2N_2$. Computed %: N 11.86.

The white hydrochloride turned very pink when left to stand exposed to the air. M.p. 215-216° with decomposition; it is freely soluble in water.

3.230 mg substance: 0.255 ml N_2 (21°, 768 mm). 3.368 mg substance: 0.265 ml N_2 (19°, 768 mm). Found %: N 9.26, 9.29. $C_{13}H_{22}O_2N_2Cl_2$. Computed %: N 9.06.

SUMMARY

1. 2-Hydroxy-5-nitrobenzyldiethylamine, synthesized by us by the Mannich reaction - from p-nitrophenol, formaldehyde, and diethylamine, as well as by reacting 2-hydroxy-5-nitrobenzyl chloride with diethylamine, is not the same as the 2-hydroxy-5-nitrobenzyldiethylamine described by Einhorn.

2. It has been proved that the product described by Einhorn as 2-hydroxy-5-nitrobenzyldiethylamine is actually 3-diethylaminomethyl-5-nitrosaligenin methylene ether.

3. A method is outlined for preparing 3-chloromethyl-5-nitrosaligenin methylene ether and for using it to synthesize 3-diethylaminomethyl-5-nitrosaligenin methylene ether.

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THE INTRAMOLECULAR HYDROGEN BOND AND THE COLOR OF ORGANIC COMPOUNDS

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As a rule, disubstituted benzenes that contain a nitro, nitroso, or acyl group adjacent (in the ortho position) to a hydroxyl group are greenish-yellow or yellow at room temperature [1], in contrast to their colorless meta and para isomers and to the monosubstituted benzenes: phenol, nitrobenzene [2], benzaldehyde, benzophenone, etc. The same is true of the corresponding ortho or peri-substituted naphthalenes and phenanthrenes. Thus, 2-acetylnaphthol-1 is yellow, while 4-acetylnaphthol-1 is colorless [3]; 2-nitrosonaphthol-1 is yellow, while 4-nitrosonaphthol-1 is colorless [4]; and 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene is light yellow, while 2--hydroxy-7-acetyl-9,10-dihydrophenanthrene is colorless [5].

This sort of relationship also exists in polysubstituted aromatic compounds: 4-nitro-2-chloro-3-hydroxylbenzaldehyde is dark-yellow [6]; 4-nitro-6-chloro-3-hydroxybenzaldehyde is dark-yellow; 2-nitro-4-chloro-3-hydroxybenzaldehyde is yellow; 2-nitro-6-chloro-3-hydroxybenzaldehyde is yellow; 6-nitro-2-chloro-3-hydroxybenzaldehyde is colorless; 6-nitro-4-chloro-3-hydroxybenzaldehyde is colorless; 1-hydroxy-2-methylanthranone-9 is yellow [7]; 1-hydroxy-3-methylanthranone-9 is colorless; 4-hydroxy-2-methylanthranone-9 is colorless; and 4-hydroxy-3-methylanthranone-9 is colorless.

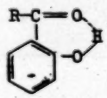
Of polysubstituted compounds containing two hydroxyl groups, only those isomers in which at least one of the hydroxyl groups is adjacent to the groups listed above (2,3-, 2,4-, 2,5- and 2,6-dihydroxy derivatives) are yellow, as a rule, while their isomers which are 3,4-, 3,5-, 3,5'- and 4,4'-dihydroxy derivatives are colorless. Thus, 2,3-dihydroxynitrobenzene is yellow; 2,4-dihydroxynitrobenzene is lemon-yellow; 2,5-dihydroxynitrobenzene is yellow; 2,6-dihydroxynitrobenzene is orange-yellow; 3,4-dihydroxynitrobenzene is nearly colorless; 3,5-dihydroxynitrobenzene is colorless; 2,3-dihydroxyacetophenone is yellow; 2,4-dihydroxyacetophenone is yellow; 2,5-dihydroxyacetophenone is light yellow; 2,6-dihydroxyacetophenone is an intense yellow; and 3,5-dihydroxyacetophenone is colorless. The same is true of compounds with a single hydroxyl group, but containing, say, two nitro groups; here, two, the isomers in which at least one of the nitro groups is adjacent to the hydroxyl group (2,3-, 2,4-, 2,5-, and 2,6-dinitrophenols) are colored, while the 3,4- and 3,5-dinitrophenols are colorless.

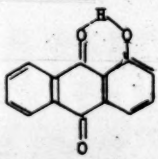
The manifestation of color is due to the same cause in all the compounds listed, no matter how different they may be. Evidently, nitro, nitroso, and acyl groups constitute a chromophoric group together with an adjacent hydroxyl group, which shifts absorption into the visible region of the spectrum. A shift of the absorption band toward the longer wavelengths when such a chromophoric group is present is also found in compounds that are already colored as a result of the presence of other groups. What then happens is a superposition, as it were, of the effects of two chromophoric groups.

Thus, all the unsubstituted para quinones are yellow. Introducing an alkyl, aryl, halogen, carboxyl, alkoxyl, nitrilo or nitro group into a quinone at any position causes no significant change in the yellow color of the initial substance.

But introducing hydroxyl (say, into anthraquinone) produces varying optical effects, depending upon the position at which it enters. When hydroxyl enters at the 2, 3, 6, or 7 position, it causes no essential change in the yellow color of the orignal compound. But when the hydroxyl group is added at one of the peri positions to the carbonyl groups of the quinoid nucleus, we get compounds that are orange, reddish-yellow, or orange-yellow, as a rule.* Introducing another hydroxyl group into 1(5)-hydroxyanthraquinone at the 2, 3, 6, or 7 position does not affect its orange color appreciably. Nor is the color noticeably darkened when the second hydroxyl group is added at the 8(4) position. The color is deepened appreciably when the hydroxyl groups are in the peri positions to the two carbonyl groups: 1,4-dihydroxy derivatives are actually red (often dark-red).

Most of the efforts to explain the foregoing optical influence of the grouping consisting of a hydroxyl group adjacent to a nitro-, nitroso-, or carbonyl group – a phenomenon that V. Meyer [1] called "extremely remarkable" – boil down to the supposition that the compound has an ortho-quinoid structure [9] or to the assumption of benzoid-quinoid tautomerism [7]. Concepts of this sort do not explain such characteristic properties of these compounds, however, as the absence of a hydroxyl band in their infrared spectrum, their (comparatively) high volatility, etc. Much closer to the truth, no doubt, is the hypothesis [10] that in these cases the shift of the absorption band toward the longer wavelengths is due to the formation of an intramolecular bond of the following type:





This provides an explanation of the fact that the singularities noted above disappear when such groups as CN or $CH_2CH_2COCH_3$ are in close proximity to the hydroxyl group; though these groups can associate with the hydrogen of the adjacent hydroxyl group, they cannot enter into intramolecular association for steric reasons, as we know from other data. This standpoint likewise provides a satisfactory explanation of the fact that, in contrast to the usual effects observed in the etherification or acylation of hydroxyl groups (preservation of the color of the original hydroxy compound), the etherification or acylation of a hydroxyl group adjacent to a nitro, nitroso, or acyl group causes either the decolorization of the original substance or a marked weakening of its color. This selective effect is strikingly evidenced in the esterification or etherification of compounds that contain diverse hydroxyl groups (mixed-associated compounds), such as [11]:

2,3-Dihydroxynitrobenzene is yellow; 2-hydroxy-3-methoxynitrobenzene is orange; 2,3-dimethoxynitrobenzene is colorless; 2,4-dihydroxynitrobenzene is lemon-yellow; 2-hydroxy-4-methoxynitrobenzene is yellow; 2-methoxy-4-hydroxynitrobenzene is colorless; 2,4-dimethoxynitrobenzene is colorless; 2-hydroxy-4-benzoylhydroxynitrobenzene is yellow; 2-benzoylhydroxy-4-hydroxynitrobenzene is colorless; 1,2-dihydroxyanthraquinone is orange-red; 1-hydroxy-2-methoxyanthraquinone is orange; 1-methoxy-2-hydroxyanthraquinone is yellow; 1-hydroxy-2-benzoylhydroxyanthraquinone is orange-yellow; 1,2-dimethoxyanthraquinone is yellow; 1-benzoylhydroxy-2-methoxyanthraquinone is yellow; 1,2-dihydroxy-4-bromothioxanthone is orange; 1-hydroxy-2-methoxy-4-bromothioxanthone is orange; 1-methoxy-2-hydroxy-4-bromothioxanthone is yellow; 1,2-dimethoxy-4-bromothioxanthone is yellow.

*2,3-, 2,6-, and 2,7-dihydroxyanthraquinones are yellow, like unsubstituted anthraquinone.

Etherification or acylation of a hydroxyl group that is not adjacent to a nitro, nitroso, or carbonyl group causes no change in the color of the original compound. But when an ortho or peri-hydroxyl group is etherified or esterified, the compound either loses its color or its color is markedly weakened.

The rules established above, which can be dealt with quantitatively only after study and comparison of absorption spectra in the visible region of the spectrum, nevertheless cast doubt upon the existence of a yellow color in some o-methoxynitro or acyl derivatives of benzene [12] or in 1-propyl-2-naphthol, 2-propylphenol, 4-nitro-5,8-dihydronaphthol-1 [13], and others. In these cases, the yellow color is apparently due to impurities (evidence of which is the wide boiling point or melting point range in many instances) or to chemical changes occurring in the air.

On the other hand, it may be assumed that the color of some hydroxyflavones is caused by the formation of an intramolecular hydrogen bond between the carbonyl group in the flavone ring and the hydrogen atom in the hydroxyl group.

SUMMARY

1. It has been established that the color of a very large number of organic compounds is caused by the presence of an intramolecular hydrogen bond.

2. The effect of superposition of "chromophoric" groups has been discovered.

3. The example of mixed-associated compounds has been used to demonstrate the selectivity of the optical effect of etherification and esterification of hydroxyl groups.

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THE CONVERSION OF ASYMMETRICAL DIMETHYLDIPHENYLBUTYNEDIOL IN AN ACID MEDIUM

III. CONDENSATION WITH PHENOL IN THE PRESENCE OF SULFANILIC ACID

Yu. S. Zalkind* and V. I. Ryabtseva

The addition of phenol at the triple bond of an acetylenic γ-glycol in the presence of sulfanilic acid was first observed by V.K.Teterin during an attempt to synthesize the phenyl ester of tetraphenylbutynediol. This reaction has been studied exhaustively by Yu.S.Zalkind, V.K.Teterin, and S.G.Kuznetsov [1].

It was learned that the addition of the phenol takes place both by the formation of a phenoxy group and at the expense of the active para and ortho carbon atoms. After the phenol has been added at the expense of the hydroxyl group, the reaction may continue along two lines: either by splitting out a molecule of water and ring closure, giving rise to 2,2,5,5-tetraphenyl-2-phenoxydihydrofuran-2,5, or the primary condensation product is isomerized to an indene derivative, which loses two molecules of water and forms a colored compound of the benzofulvene series.

A similar phenomenon occurs when phenol is added at the para carbon atom.

The products of the addition of phenol at the ortho carbon atom occupy a special place. The ortho position of the hydroxyl group in the addition product made further cyclization possible, a chroman ring being constituted.

Yu.S.Zalkind and O.F.Moiseeva [2] subsequently extended their investigation of the condensation of acetylenic γ-glycols to tetramethylbutynediol. Here the reaction is confined to the formation of two derivatives of dihydrofuran with phenoxy and p-hydroxyphenyl groups as substituents at the ring's double bond. The phenol is not added at the ortho carbon atom.

We were interested in finding out in what way and with what subsequent transformations phenol would condense with an asymmetrical acetylenic γ-glycol [3] – 2-methyl-5,5-diphenylpentyne-3-diol-2,5 (I).

The condensation was effected by the Teterin method [4]: heating a mixture of the glycol, phenol, and sulfanilic acid in anhydrous benzene, to allow for the water evolved during the course of the reaction.

The ease with which phenol condenses with as-dimethyldiphenylbutynediol, the absence of tarring, and the evolution of exactly one molecule of water per molecule of the glycol are all worthy of note.

The condensation products were two colorless isomeric crystalline substances, with the empirical formula of $C_{24}H_{22}O_2$.

The bulk of the product was a substance with a m.p. of 125° (II), its yields being as high as 85% of the theoretical. This substance is freely soluble in

*Deceased.

ether, benzene, and petroleum ether; it is somewhat less soluble in acetone, alcohol, and ethyl acetate, and it is soluble in glacial acetic acid only when heated.

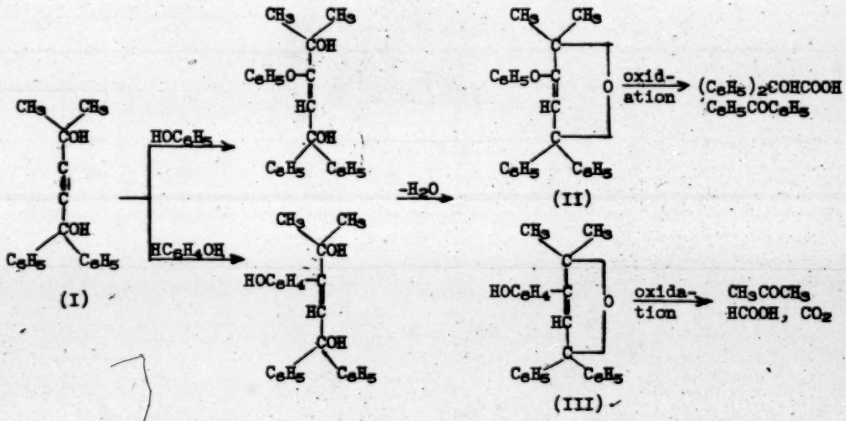
The molecular weight and the percentage composition of this substance are evidence that one molecule of phenol has been added to one molecule of the glycol and one molecule of water has been evolved. The presence of the phenoxy group, which was split off by boiling with hydriodic acid and identified via tribromophenol, was proof that the phenol was added to the glycol at a carbon atom, while the absence of active hydrogen, like the absence of a double bond in the open chain, evidenced the feasibility of closing the dihydrofuran ring; no colored products, such as could be produced if the phenol group were adjacent to phenyl radicals [1], were found. This led us to assume that the phenoxy group was added to the carbon atom adjacent to the methylated carbon atom.

All these facts led us to assign the structure of 2,2-dimethyl-5,5-diphenyl--3-phenoxydihydrofuran-2,5 (II) to the substance with a m.p. of 125°.

The other condensation product of as-dimethyldiphenylbutynediol with phenol, with a m.p. of 166° (III), exhibited a hydroxyl group; hence, the substituent at the double bond in the ring was a hydroxyphenyl group. We may therefore assign the structure of 2,2-dimethyl-5,5-diphenyl-3-hydroxyphenyldihydrofuran-2,5 (III) to the substance with a m.p. of 166°. This substance is freely soluble in nearly all the usual solvents. We were able to recrystallize it from toluene.

Thus, the addition of phenol to as-dimethyldiphenylbutynediol is similar to the addition of phenol to tetramethylbutynediol (Diagram I).

Diagram I



The small quantity of the substance with a m.p. of 166° (III) recovered – all we could get was some 0.5 g – made it impossible to determine experimentally whether the phenol is added at the para or ortho carbon atom. But, by analogy with tetramethylbutynediol [2], it may be assumed that the substituent at the ring double bond in this substance will be a parahydroxyphenyl group.

The substance with a m.p. of 125° (II) was oxidized to identify its structure. Its extraordinary resistance to oxidation in an acid medium was noteworthy.

Chromic anhydride dissolved in acetic acid oxidized only a negligible portion of the substance, even at 100°, but then the oxidation of the primary products is more vigorous than that of the initial substance, nothing but acetone and traces of formic acid and carbon dioxide being recovered.

Oxidation with potassium permanganate dissolved in acetone, with considerable quantities of caustic potash present, is much better. Here the acid products of oxidation included benzilic acid, while the neutral products included benzophenone, identified via its semicarbazone.

The oxidation products do not contradict the structure assigned to the substance with a m.p. of 125°, though they do not fix the position of the phenoxy group within the dihydrofuran ring.

The position of the phenoxy group was determined by hydrolyzing the substance under conditions resembling those used for the hydrolysis of 2,2-dimethyl--5,5-diphenyl-3-ethoxydihydrofuran-2,5, described in our second report [5]. Here, too, we secured 2,2-dimethyl-5,5-diphenyltetrahydrofuran-2,5, with a m.p. of 66-67° [8] plus phenol.

Thus, we may state it as experimentally proven that in the substance with a m.p. of 125° (II), the phenoxy group occupies the same position in the dihydrofuran ring as that occupied by the ethoxy group in the corresponding ethoxy derivative.

EXPERIMENTAL

1) Condensation of as-dimethyldiphenylbutynediol with phenol in the presence of sulfanilic acid.

A mixture of 18.8 g of phenol, 40 ml of benzene, and 0.2 g of sulfanilic acid was heated to boiling to check whether any moisture was present. Then 13.3 g of the glycol was added, and heating was continued. The mixture boiled at 88.5°. almost immediately beginning to evolve water, which was collected in a trap. The reaction was stopped after 1.5 hours of boiling. The amount of water evolved was exactly one molecule per molecule of glycol.

The sulfanilic acid was filtered out of the golden-yellow solution and treated with steam until no more phenol could be detected in the distillate (ferric-chloride test).

The brittle, easily fusible golden mass left behind after the solvent and the excess phenol had been driven off was treated with twice its weight of alcohol heated to 60-70°. Upon cooling, the alcohol, together with a small amount of tar dissolved in it, was suction-filtered out of the pasty mass, the residual colorless crystals being purified by recrystallization from alcohol and ethyl acetate, after which they fused at 125°.

In the last two tests, crystals with a higher melting point than that of the first substance were recovered from the mother liquor after the first substance had been crystallized from alcohol. They fused at 166° after recrystallization from toluene.

2) 2,2-Dimethyl-5,5-diphenyl-3-phenoxydihydrofuran-2,5 (II).

Analysis of the substance with a m.p. of 125°: 0.1565 g substance: 0.4846 g CO_2; 0.0900 g H_2O. 0.1171 g substance: 0.3623 g CO_2; 0.0682 g H_2O. Found %: C 84.53, 84.35; H 6.64, 6.43. $C_{24}H_{22}O_2$. Computed %: C 84.20; H 6.43.

Determination of the molecular weight ebullioscopically in acetone: 0.2452 g substance: 9.95 g acetone: Δt 0.13°; 0.7232 g substance: 9.59 g acetone: Δt 0.40°. Found: M 341, 344. $C_{24}H_{22}O_2$. Computed M 342.

Qualitative determination of the phenoxy group: A mixture of 1 g of the substance with a m.p. of 125° and 75 g of hydriodic acid was boiled with a reflux condenser for 7 hours, after which the whole mixture was steam-distilled. The iodine contained in the distillate was combined with hyposulfite, and bromine water was added to the solution. The flocculent white precipitate was recrystallized from alcohol and dried in a desiccator, after which it fused at 94° and exhibited no depression of the melting point when mixed with known tribromophenol.

The Chugaev-Tserevitinov reaction for a hydroxyl group was negative for the substance with a m.p. of 125°.

The results of oxidizing the substance with a m.p. of 125° are listed in the subjoined table.

Expt. No.	Amount of substance used, g	Oxidant, g	Solvent, ml	Experimental conditions	Amount of substance not oxidized, g	Oxidation products	
						Neutral	Acid
1	7	$KMnO_4$ (4.8)	Acetone, 50	Heating to a boil for 40 hours with a reflux condenser	6.8	–	–
2	5	CrO_3 (4.5)	Glacial CH_3COOH, 100	Heating for 20 hours to 50-70°, with stirring	4.5	Acetone	HCOOH, CO_2
3	5	Ditto	Ditto	50% solution of the substance and the oxidant heated to a boil and decanted together	4.5	–	–
4	6	$KMnO_4$ (8) 40% KOH 25 ml	Acetone, 100	Heating to 55-60° with a reflux condenser and stirring	Approx. 5	Benzophenone	Benzilic acid

Hydrolysis of the substance with a m.p. of 125°: 1 g of the substance, 8 ml of ethyl alcohol, 2 ml of water, and 1 ml of concentrated sulfuric acid were heated with a reflux condenser over a boiling water bath for 4 hours.

After the solution, which smelled strongly of phenol, had cooled, colorless crystals settled out within the course of a few hours; they fused at 66-67° after having been recrystallized from alcohol and proved to be the same as 2,2-dimethyl-5,5-diphenylfuranone-3 (mixed sample and production of the semicarbazone).

3) 2,2-Dimethyl-5,5-diphenyl-3-hydroxyphenyldihydrofuran-2,5 (III).

Analysis of the substance with a m.p. of 166°: 0.1000 g substance: 0.3077 g CO_2; 0.0569 g H_2O. Found %: C 84.00; H 6.30. $C_{24}H_{22}O_2$. Computed %: C 84.20; H 6.43.

Determination of the number of hydroxyl groups by the Chugaev-Tserevitinov method: 0.1024 g substance: 8.2 ml CH_4 (19°, 752 mm). Found: CH_4 7.1 ml. OH 5.18 %: $C_{24}H_{21}O(OH)$. Computed: CH_4 6.7 ml; % OH 4.97.

SUMMARY

1. As-dimethyldiphenylbutynediol has been condensed with phenol in the presence of sulfanilic acid, and the condensation products were analyzed.

2. It has been found that phenol is readily added at the triple bond to dimethyldiphenylbutynediol, one molecule of water being split out and the dihydrofuran ring being closed; this results in the formation of two substances of the dihydrofuran series: 2,2-dimethyl-5,5-diphenyl-3-phenoxydihydrofuran-2,5, with a m.p. of 125°; and 2,2-dimethyl-5,5-diphenyl-3-hydroxyphenyldihydrofuran-2,5, with a m.p. of 166°.

3. It has been found that the phenol is added mainly at the oxygen atom, only a very minor proportion being added at the para carbon atom.

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OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XII. THE HYDROLYTIC CLEAVAGE OF 2-PYRIDINE-3(1)-OXY-1,4(3,4)-NAPHTHOQUINONE BETAINE*

D. P. Vitkovsky and M. M. Shemyakin

The present paper reports the results of our researches on the conditions and nature of the hydrolytic cleavage of the rings in 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine (I), which may be readily prepared by condensing 2,3-dichloro-1,4-naphthoquinone with pyridine [1]. 2-Pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine cannot be classed as either a para or an ortho quinone, inasmuch as its structure cannot be satisfactorily described by either one of the structural formulas (IA) and (IB) alone.

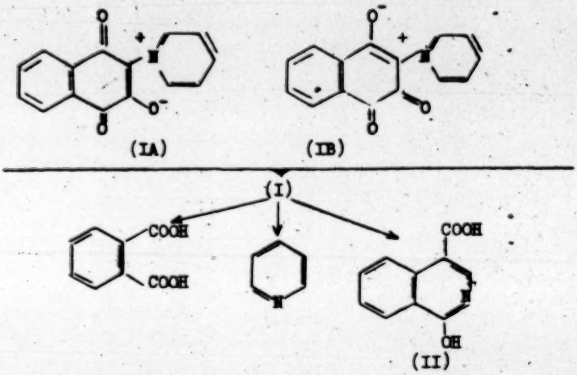
It was therefore essential to learn which of the carbon bonds in the quinone ring of this compound would be ruptured by hydrolyzing agents, and under what conditions this could be carried out. The secondary processes that the primary cleavage products of this quinone may undergo also merited investigation. We expected that this quinone would hydrolyze only under rather severe conditions, since the presence in its molecule of an electrovalent bond between the oxygen atom of the ionized hydroxyl group and the nitrogen atom of the pyridine ring ought to diminish the polarization of the carbon bond subject to cleavage, thus exerting a negative effect upon processes of this sort, even though each of these substituents, taken by itself, is usually able to polarize carbon bonds rather highly and hence facilitate their hydrolytic cleavage (cf [2,3] as well as our following report). It was actually found that 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone resists the action of hydrolyzing agents rather well. It remains practically unaffected after as much as 50 hours of boiling with an aqueous buffer solution with a pH of 7.5, slowly beginning to change only at higher pH values of the solution (approximately 9.5). Practically speaking, it can be hydrolytically cleaved only under very much more severe conditions, viz.: boiling this quinone for a long time with a 1% aqueous solution of caustic soda, and even then the solution has to be boiled for 48 to 50 hours for the reaction to be approximately 80% complete.

This process must be carried out with no atmospheric oxygen present, since otherwise the hydrolytic reactions are paralleled by other transformations that are of an oxidative-hydrolytic nature.** When the reaction is carried out with no atmospheric oxygen present, the same end products are always secured, no matter how alkaline the medium, viz.: phthalic acid (maximum yield about 50%), pyridine (maximum yield about 30%), and 1-hydroxy-4-carboxyisoquinoline (II) (maximum yield about 20%).***

*Report X on the hydrolytic cleavage of carbon bonds.

**Cf dissertation by D. P. Vitkovsky, Moscow (1948).

***In addition one can secure negligible quantities of still another substance (m.p. 168-170°), the structure of which is as yet undetermined. Besides the individual compounds listed above, a fairly large quantity of tarry substances is also produced, which cannot be separated or purified.



(II)

Isolating these reaction products involved no great complexities, but considerable effort had to be spent upon identifying the structure of the compound (II), since it was rather hard to foresee the possibility of its production in this reaction. As will be shown below, however, it is the formation of this very substance that enables us to comprehend not only the nature of the process involved in the hydrolytic cleavage of the rings in the initial quinone, but also the mechanism involved in the secondary transformations, which proved to be similar to the analogous reactions that we have described earlier and that are typical of this group of quinones.

Compound (II) is a white crystalline substance that melts with decomposition at 295-296°. We proved its structure as follows: The composition of this substance corresponded to the empirical formula $C_{10}H_7O_3N$. It contained a single carboxyl group, readily formed a slightly soluble silver salt, and yielded an ethyl ester with a m.p. of 226-227° when heated with ethyl alcohol and sulfuric acid. The results of its distillation with zinc dust were of fundamental importance in demonstrating the structure of the compound we had isolated. The principal product of this reaction was isoquinoline, which was isolated and identified as its picrate. Even more fundamental was the decarboxylation of the above-mentioned silver salt, which, in addition to confirming the basic skeleton of the substance, also proved the existence and the position of a hydroxyl group in its molecule, since we here recovered isocarbostyril, the yield of which was almost quantitative. It followed that the substance we had synthesized was a derivative of isoquinoline, containing a hydroxyl group at the 1 position. Thus the only thing still uncertain was the position of the carboxyl group.

1-Hydroxy-4-carboxyisoquinoline, with a m.p. of 290°, its ethyl ester having a m.p. of 227°, has been described in the literature a long time ago, [4]. The compounds we had prepared had similar melting points. It therefore seemed quite likely that our acid was actually 1-hydroxy-4-carboxyisoquinoline. This question was resolved by synthesizing the latter compound and its ester by the method described in the literature [4]; we found that their properties were wholly identical with those of the acid we had synthesized and of its ethyl ester. Hence, the substance with a decomp. temp. of 295-296° produced by the hydrolytic cleavage of 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone (I) betaine actually possesses the structure represented by Formula (II).

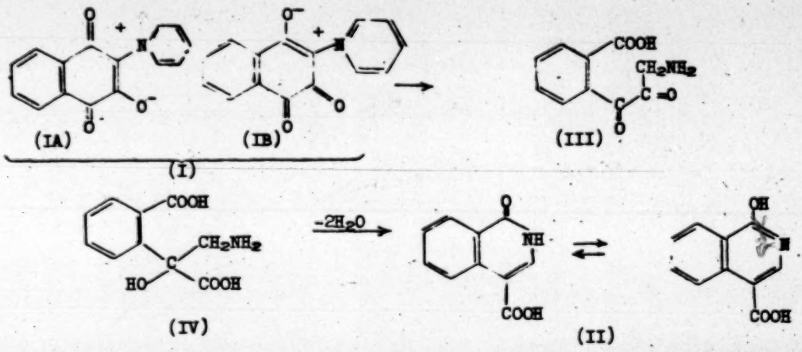
When we compare the structure of the original quinone (I) with that of the end product, 1-hydroxy-4-carboxyisoquinoline (II), the transformations we have

discovered may seem quite paradoxical at first glance, though they can be readily explained, both as regards their separate stages and as a whole. The first thing we must remember is the fact that these transformations take place only under the action of water and OH'. Second, it must be emphasized that both the pyridine ring and the quinone ring in the original quinone molecule (I) may be hydrolytically cleaved simultaneously or successively by the action of these very factors. Indeed, it is well known (cf [5-8], for instance) than in an alkaline medium the ring may be ruptured in pyridine bases whenever the radical attached to the nitrogen atom can polarize the $-N=C<$ bond of the ring sufficiently. As a rule, the end products of these conversions are glutaconaldehyde (or a compound formed as the result of the latter's subsequent changes) and the corresponding amine or amide. In our case, the radical attached to the nitrogen atom is the oxynaphthoquinone ring, the carbonyl groups of which must undoubtedly cause it to exert a powerful polarizing effect upon the $-N=C<$ bond of the pyridine ring. We carried out the reaction in a boiling 1% aqueous solution of caustic soda. Hence, both the structural peculiarities of the quinone molecule (I) and the external conditions of our reaction must promote the hydrolytic cleavage of the pyridine ring in this quinone, this cleavage necessarily ending in the formation of the corresponding amino compound. On the other hand, we know [2,9] that one of the characteristics of 2-oxyquinones, whose structure resembles that of the quinone (I), is the tendency of their ring systems to undergo hydrolytic cleavage under certain conditions. This usually occurs after prolonged heating of their solutions in aqueous alkalies, the quinone molecule first being hydrated, and then its ring being ruptured. It is evident that this type of cleavage is possible in our case as well. Thus, under the conditions prevailing in our reaction we must expect cleavage of the quinone ring as well as of the pyridine ring. As we have said above, the second of these processes results in the formation of an amino group. The first process could, in general, result in the rupture of the bond between the 1 and 2, 2 and 3, or 3 and 4 carbon atoms of the quinone ring. The structure of the end product – 1-hydroxy-4-carboxyisoquinoline (II) makes the latter two reactions quite impossible, however. Hence, the aggregate effect of these two processes can only be the formation of the intermediate compound (III).

This type of quinone cleavage, resulting in the formation of intermediate α-diketones whose structure resembles that of Compound (III), has been described previously, viz.: for several 3,6-disubstituted 2,5-dioxybenzoquinones [10-12]. This further confirms the correctness of our assumption that the aminodiketocarboxylic acid (III) must be an intermediate stage in the conversion of the original quinone (I) into the final 1-hydroxy-4-carboxyisoquinoline (II).

Now let us consider the ensuing stages of these transformations, involving the subsequent changes in Compound (III). In the investigations of the cleavage of substituted 2,5-dioxybenzoquinones it was found [10-12] that the α-diketones formed as a result of the rupture of the ring systems of these quinones usually undergo a "benzilic acid" rearrangement at the very instant they are formed, being converted into the respective α-hydroxy acids by heating with aqueous solutions of alkalies. It is quite obvious that the same sort of rearrangement may also take place in our case, leading to the formation of the amino hydroxy carboxylic acid (IV), which is then converted into 1-hydroxy-4-carboxyisoquinoline (II). As for the last stage – the ring closure of Compound (IV) to form the isoquinoline derivative (II) – it does not require detailed consideration, inasmuch as similar transformations have been successfully investigated in the isocoumarin series. The closest example is the formation of the same isoquinoline derivative (II) from isocoumarin-4-carboxylic acid and from the ester of the hydroxymethylenehomophthalic acid [4]. It should merely be remembered that the conversion of Compound (IV) into the final 1-hydroxy-4-carboxyisoquinoline (II) is accompanied by the splitting out of two molecules of water – one during the ring-closure

process, and the other during the formation of a double bond in the same ring.



Thus the formation of 1-hydroxy-4-carboxyisoquinoline (II) from 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine (I), which seems so unexpected at first glance, is quite regular. The peculiarity of these observed transformations is due to the fact that the original quinone is also a pyridine base. It must be remembered, moreover, that much of the original quinone undergoes thoroughgoing changes in addition to the reactions we have discussed, which lead to the formation of appreciable quantities of phthalic acid and pyridine in addition to the Compound (II) (vide supra). This indicates that the pyridine ring of the quinone (I) is harder to rupture than the quinone ring. It should likewise be stressed again that the secondary reactions involved in the "benzilic acid" rearrangement must not be regarded as rare exceptions, but as one of the types of secondary transformations that may occur during the hydrolytic cleavage of benzene or naphthalene oxyquinones. Apparently, this type of transformation may occur whenever the ring system of the original oxyquinone is ruptured between the 1 and 2 carbon atoms, resulting in the formation of the respective substituted α-diketones as the primary reaction product.

EXPERIMENTAL*

Hydrolytic Cleavage of 2-Pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone (I)

a) In a 1% solution of caustic soda. The reaction was carried out in a two-necked 3-liter flask fitted with a reflux condenser, and a tube reaching to the bottom of the flask, through which hydrogen, which had first been passed through a solution of lead acetate, alkaline solutions of potassium permanganate and pyrogallol, concentrated sulfuric acid, and a layer of copper heated to 300-400°, entered throughout the experiment. After leaving the flask, the hydrogen passed through the reflux condenser and then through two Tishchenko bottles, the first one (A) containing 10% sulfuric acid, and the second (B) containing an alkaline solution of pyrogallol. Into the flask we poured 1.5 liters of a 1% solution of caustic soda, the quinone (2.50 g) being placed in a glass vessel located above the level of the liquid and suspended from the hook of a glass rod that was inserted through the stopper of the flask. The airtightness of the system was checked, and then the solution was heated to a boil, a slight current of hydrogen being passed through the solution uninterruptedly. Four hours later the vessel containing the quinone was immersed in the caustic soda solution, and boiling was continued for 48 hours, without stopping the flow of hydrogen. The substance dissolved rapidly, turning the solution orange, the color gradually

*The analytical section of this research was carried out with the assistance of E. A. Ignatyeva, to whom we are deeply grateful.

changing to dark brown. After 48 hours had elapsed, the solution was cooled in a stream of hydrogen, the solution pH was raised to 7.0 by adding sulfuric acid, the reflux condenser was replaced by a straight-flow one, the air was again forced out by hydrogen for 2 hours, and then the solution was evaporated to about 100 ml. The precipitated silicic acid[4] was filtered out and boiled three times with water, and the aqueous filtrates were combined with the reaction solution and extracted with chloroform. The chloroform extract was desiccated with calcium chloride, and the solvent was driven off to dryness. This left 1.43 g of a tarry substance, which yielded 0.5 g (20%) of the original quinone with a m.p. of 292° after recrystallization from water.

After having been extracted with chloroform, the aqueous reaction solution was acidulated with sulfuric acid until its reaction with Congo red was acid. A brown deposit settled out, which was filtered out, washed with water, and dried. Weight 0.53 g. Double recrystallization from glacial acetic acid and activated charcoal yielded 0.27 g (18%) of 1-hydroxy-4-carboxyisoquinoline, which melted with decomposition at 295-296° (see below for the proof of the structure of this compound).

The acid reaction solution was again extracted with chloroform. The extract was desiccated with calcium chloride, and the chloroform was driven off until the residual volume was 2-3 ml. A white crystalline precipitate gradually settled out; it was filtered out and washed with chloroform. This yielded 0.07 g of a substance with a m.p. of 168-170°. It was crystallized from water as elongated needles with a m.p. of 91-92°. It contained no nitrogen. We made no further investigation of this compound.

The reaction solution was again strongly acidulated with sulfuric acid and extracted with ether. The extract was desiccated with sodium sulfate, and the ether was driven off to dryness. There was left 0.65 g (49%) of phthalic acid, which was purified by repeated recrystallization from water with activated charcoal present.

The solution of sulfuric acid in bottle (A) (see above) was alkalinized, and then about half the liquid contents were driven off. The distillate contained pyridine, which was precipitated as the coordination compound $(CuPy_2)(CNS)_2$ by a solution of copper sulfate and then titrated with a solution of potassium thiocyanate. The excess of the latter was titrated back with a solution of silver nitrate [13]. We found 0.1890 g (30%) of pyridine. The pyridine was also identified as its picrate (m.p. 74°).

b) In a buffer solution with a pH of 7.48. The reaction was carried out under conditions similar to those described in Experiment (a). We used 2.50 g of the quinone (I) and 1.5 liters of a phosphate buffer solution. This yielded 2.40 g (96%) of the original quinone, 0.016 g of pyridine, 0.0202 g of phthalic acid (determined by the method described in our Report II [14]), and traces of 1-hydroxy-4-carboxyisoquinoline.

c) In a buffer solution with a pH of 9.30. The conditions under which the reaction was carried out resembled those described for Experiment (a). We used 2.50 g of the quinone (I) and 1.5 liters of borate buffer solution. This yielded 2.30 g (92%) of the original quinone, 0.013 g of pyridine, 0.0472 g of phthalic acid, and 0.0166 g of 1-hydroxy-4-carboxyisoquinoline.

Investigation of the Properties and Proof of the Structure of the Substance With a Decomposition Temperature of 295-296°.

This substance crystallized from glacial acetic acid or alcohol as colorless acicular needles with a temp. decomp. of 295-296°. It was insoluble in water or

[4] Silicic acid was produced in appreciable quantities as the result of the action of the alkaline solution upon the surface of the glass flask.

mineral acids, though soluble in an aqueous soda solution, and was recovered unchanged as a jellylike white precipitate when the latter was acidulated. Silver nitrate precipitated a water-insoluble silver salt from an aqueous solution of its ammonium salt.

Found %: C 63.61; H 3.73; N 7.70. $C_{10}H_7O_3N$. Computed %: C 63.49; H 3.70; N 7.41. Data of back titration: Found M 190. $(C_6H_6ON)COOH$. Computed: M 189.

a) Conversion into isoquinoline. 0.15 g of the substance with a decomposition temperature of 295-296° was carefully mixed with 10 g of zinc dust. The mixture was heated in a long narrow test tube, the opening of which had first been closed with a stopper of absorbent cotton. Calcination was continued for 10 minutes. The reaction products settled as drops of oil on the cold walls of the test tube. They were dissolved in ether, and the ether extract was washed with a 5% alkali solution and with water, and then desiccated with sodium sulfate. Driving off the ether left behind an oily liquid with the characteristic odor of isoquinoline. It was dissolved in 5 ml of alcohol, and a solution of picric acid in 30% alcohol saturated in the cold was poured into the resultant solution. A yellow crystalline precipitate of the picrate was thrown down; it was filtered out, washed with alcohol, and recrystallized from 30% alcohol. The substance fused at 220-221° and exhibited no depression of the melting point when mixed with isoquinoline picrate.

b) Conversion into isocarbostyril. 1.0 g of the substance with a decomposition temp. of 295-296° was dissolved in 1.5 ml of dilute ammonia solution, the excess of the latter being neutralized by carefully adding nitric acid. A 5% solution of silver nitrate was added to the resulting solution until all the resultant silver salt had been thrown down. The latter was filtered out, washed with water, alcohol, and ether, and then desiccated for 1 hour at 60° and 5 mm. The silver salt (1.1 g) was mixed with 2.2 g of calcined sand, and the mixture was poured into a porcelain boat, which was placed in a glass tube. One end of the tube was closed with a stopper of absorbent cotton and connected to a vacuum pump. Nitrogen was fed into the other end of the tube. After all the air had been driven out, the part of the tube in which the boat was located was heated.

The mixture turned black at first, becoming light again after a few minutes had elapsed, which indicated the end of the reaction. The crystalline reaction products settled on the cold walls of the tube. They were dissolved in hot alcohol, which was then driven off. The dry residue was triturated with 10% sodium bicarbonate solution, the portion that failed to dissolve being filtered out. Acidulation of the filtrate precipitated 0.1 g of the original acid. The substance that remained insoluble (0.45 g) was purified by recrystallizing it from alcohol. This yielded colorless needles with a m.p. of 207-208°, which fused at the same temperature when mixed with isocarbostyril. The yield was nearly quantitative.

c) Preparation of the ethyl ester of the substance with a decomposition temp. of 295-296°. 0.5 g of the substance was mixed with 50 ml of alcohol and 10 ml of concentrated sulfuric acid. The mixture was boiled for 3 hours, the substance slowly dissolving. When the solution cooled, a crystalline precipitate was thrown down in the form of elongated colorless needles. It was filtered out, washed with water, and recrystallized from alcohol. This yielded 0.3 g of a compound with a m.p. of 226-227°, which exhibited no depression of the melting point when mixed with the ethyl ester of 1-hydroxy-4-carboxyisoquinoline (m.p. 227°), which was specially synthesized by us according to the method previously described in the literature [14].

d) Identification of the substance with a decomp. temp. of 295-296° as

1-hydroxy-4-carboxyisoquinoline. 1-Hydroxy-4-carboxyisoquinoline was prepared by the method described by W. Dieckmann and W.Meiser [4]. Contrary to the figures cited by these authors, the preparation we synthesized fused with decomposition at 295-296°, rather than at 290°; it exhibited no depression of the melting point when mixed with the compound prepared by hydrolytically cleaving 2-pyridine-3(1)--oxy-1,4(3,4)-naphthoquinone betaine (I).

SUMMARY

A study has been made of the conditions and the nature of the hydrolytic cleavage of 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine. It has been found that it can be cleaved hydrolytically when boiled for a long time in an aqueous alkaline solution, phthalic acid, pyridine, and 1-hydroxy-4-carboxyisoquinoline being recovered as the end products of this reaction. It has been shown that the formation of the last compound involves the hydrolytic cleavage of the pyridine ring as well as the quinone ring of the original quinone, as a result of which there is first formed an aminodiketocarboxylic acid (III), which undergoes a further "benzilic acid" rearrangement, being converted into the corresponding amino hydroxy carboxylic acid (IV), which then suffers ring closure to the final product, 1-hydroxy-4-carboxyisoquinoline, two molecules of water being split out.

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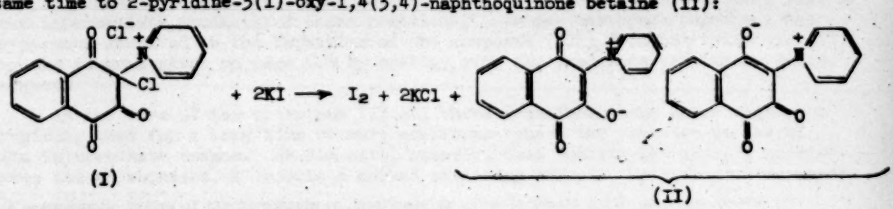
OXIDATIVE AND OXIDATIVE-HYDROLYTIC TRANSFORMATIONS OF ORGANIC MOLECULES

XIII. THE HYDROLYTIC CLEAVAGE OF 2-CHLORO-2-PYRIDINE-1,2,3,4-TETRAHYDRONAPHTHALENE-1,3,4-TRIONE CHLORIDE*

D. P. Vitkovsky and M. M. Shemyakin

A few years ago our laboratory began an investigation of the relationships existing between the structure of carbocyclic compounds and the ease with which their ring systems are hydrolytically cleaved by oxidative and hydrolyzing agents. In the course of these investigations it became essential to make a study of the hydrolytic cleavage of one of the triketones of the tetrahydronaphthalene series, namely, 2-chloro-2-pyridine-1,2,3,4-tetrahydronaphthalene-1,3,4-trione chloride (I), since it seemed to us that this compound might provide an extremely convincing demonstration of the extent of the influence of substituents upon such processes. It was expected that the triketone we had chosen would not only be readily hydrated at the double bond of the carboxylic group, at the 3 position, but would then be cleaved hydrolytically between the 2 and 3 carbon atoms. As we saw it, the latter reaction would have to occur extremely easily, inasmuch as the substituents attached to the 2 and 3 carbon atoms in the hydrated triketone molecule would polarize the bond connecting these two atoms extremely powerfully, thus greatly facilitating the cleavage of that bond by hydrolyzing agents. To provide experimental proof of this hypothesis, we also made a study of the nature of the hydrolytic cleavage of the ring system of the triketone (I) and of the conditions under which this occurs.

We synthesized the latter compound, which has not been previously described in the literature, by chlorinating 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone (II), which in turn may be readily prepared by condensing 2,3-dichloro-1,4-naphthoquinone with pyridine [1-3]. The triketone (I) is a white crystalline compound that is highly unstable in the presence of water. Its composition is given by the empirical formula $C_{15}H_8O_3NCl_2$. According to Formula (I) this substance contains one ionogen atom of chlorine, the second halogen atom being incapable of dissociation in an aqueous solution, though possessing strong oxidizing properties, which is characteristic of halogen carbonyl compounds in which the halogen atom is attached to the carbon atom linked to two carbonyl groups (cf [2]). Thus, the triketone (I) can oxidize an iodine ion to free iodine, being reduced at the same time to 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine (II):

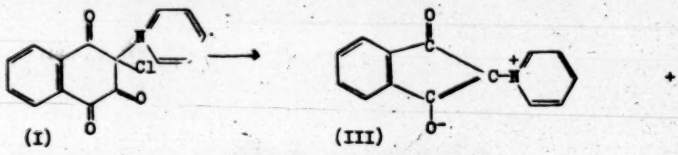


(I) (II)

*Report XI on the hydrolytic cleavage of carbon bonds.

Under certain conditions (cf. the experimental section of this paper) this betaine can be recovered at the end of the reaction, which is convincing proof that the structure expressed by Formula (I) may be attributed to the triketone we have synthesized.

As was to have been expected, the triketone (I) is cleaved with extraordinary ease by hydrolyzing agents, the hydrolytic cleavage of its ring system being usually accompanied by a series of secondary transformations, as a result of which the following compounds may be recovered as end products: 2-pyridineindenon-1(3)-ol-3(1) (III) (yield approximating 50%); pyridine (yield approximating 20%); and phthalic acid (yield approximating 12%). In addition, about 1 mol of carbon dioxide and 2 mols of hydrogen chloride are formed. These transformations, which take place fairly slowly in aqueous solution at 19-20°, occur very quickly upon heating; if the solution pH is higher than 7, they are practically instantaneous even at room temperature. The formation of all these substances does not depend upon atmospheric oxygen – they are secured even when the latter is excluded.



(I) (III)

$$+ C_6H_4(COOH)_2 + C_5H_5N + CO_2 + 2HCl$$

Compound (III) is a bright-yellow crystalline substance with a m.p. of 256-257°, which is insoluble in acids or alkalies.

Determination of its molecular weight and the results of its analysis indicate that its composition is given by the empirical formula $C_{14}H_9O_2N$. Oxidizing it with potassium permanganate yields pyridine and phthalic acid, the yield being as high as 80-85%. Some carbon dioxide is also formed.

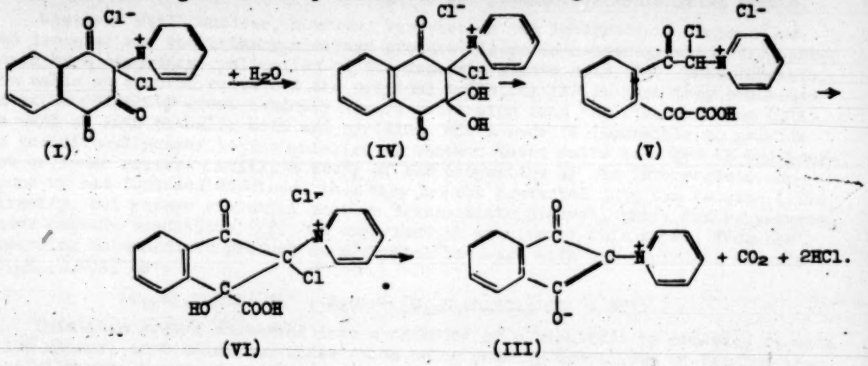
Under certain conditions (cf the experimental section of this paper) the triketone (I) may be also transformed into the sulfur analog of Compound (III) – a bright-red crystalline substance with a m.p. of 198-199°, whose composition is given by the empirical formula $C_{14}H_9ONS$. The reaction of the latter substance with lead acetate results in the replacement of its sulfur atom by an oxygen atom, thus giving an 80% yield of the compound (III).

It was certain that the transformation of the triketone (I) into the compound (III) and the latter's sulfur analog entailed the opening of its six-membered ring to begin with, followed by ring closure, but this time of an indan derivative. Such conversions of one cyclic system into another have been often described in the literature, in some cases the authors having been able to recover even some of the intermediate products of these reactions;* we may therefore represent the processes involved in the formation of the compound (III) from the triketone (I) by the diagram given on page 608 by analogy with the processes previously investigated.

In the case of the triketone (I) all these transformations occur with such rapidity that for a long time we were unable to retard the reaction at any of its intermediate stages. We did note, however, that whereas OH^- sharply accelerates these processes, H^+ exerts a marked retarding effect. This observation made

*A comprehensive review of the literature on this topic is given in Report I [4]. Also see [8-10].

it possible to recover some of the intermediate products in their individual state by appropriately varying the medium's acidity and the time the substance was kept in the solution. Unfortunately, they are all highly unstable compounds. This circumstance was a great handicap in the detailed investigation of their structure.



(I) (IV) (V) (VI) (III)

The transformation of the triketone (I) into the end compound (III) can be interrupted at one of the intermediate stages by carrying out the reaction in a 10% aqueous solution of any mineral acid. Then the original triketone (I) dissolves very quickly, after which a new crystalline substance begins to settle out almost at once; this substance is a salt that contains the anion of the mineral acid employed in the reaction. In this way we readily secured the chloride, the nitrate, and even the bisulfate, in whose molecules the chlorine atom, the nitric-acid group, and the sulfuric-acid group, respectively, can dissociate in an aqueous solution, thus being quantitatively determinable by precipitation with silver nitrate, nitron, or barium chloride. Analysis of these salts clearly showed that their formation involved the addition of a molecule of water to the original triketone (I):

$$[C_{15}H_9O_3NCl]^+Cl^- + HX + H_2O \rightarrow [C_{15}H_{11}O_4NCl]^+X^-,$$
(I) (V)

where X = Cl, NO_3, HSO_4.

Like the triketone (I), all of these salts contain a chlorine atom that possesses oxidizing properties – all of them can oxidize an iodine ion quantitatively to free iodine. In contrast to the triketone (I), however, they are not thereby reduced to 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine (II), only the compound (III) being formed. Hence (cf. [2]), the molecules of the salts we secured do not contain the carbon skeleton of the original triketone (I), and thus they are not hydration products of this triketone [Formula (IV)]. Nonetheless, these substances are doubtless salts of one of the intermediate compounds in the transformation of the triketone (I) to the final betaine (III), since they can all be converted into this betaine or into its sulfur analog under the same conditions and with practically the same yield as the triketone (I), at the same time splitting out carbon dioxide and hydrogen chloride, like the latter. Moreover, like the triketone (I), these salts can be partially cleaved to phthalic acid and pyridine.

Inasmuch as we cannot attribute the structure given by Formula (IV) to the intermediate compound we isolated in the form of various salts, its formation must involve not only the hydration, but also the hydrolytic cleavage of the ring system of the original triketone (I), which evidently occurs practically instantan-

eously when the latter compound is dissolved in the aqueous solution of a mineral acid. Thus, these results support our assumption, expressed at the beginning of this paper, that the substituents in the molecule of this triketone very greatly facilitate the latter's cleavage in the presence of hydrolyzing agents.

What was still unclear, however, was whether the intermediate compound we had isolated was the primary cleavage product (V) or an α-hydroxy acid (VI), produced by a secondary cyclization of its isomeric diketo acid (V). Unfortunately, the salts we secured resembled the original triketone (I) in that they exhibited an extraordinarily great tendency toward conversion into the final betaine (III), as well as into phthalic acid and pyridine, which made it impossible to provide an unequivocal answer to the question of whether these salts belonged to the benzene or indan series. Still, a study of the properties of the intermediate compound we had isolated disclosed that they are not converted into the betaine (III) directly, but rather via still another intermediate product, which can be secured under certain conditions (cf. the experimental section of this paper) from the preceding intermediate product as a crystalline base with the empirical formula $[C_{15}H_{11}O_4NCl]^{\cdot}OH'$:

$$[C_{15}H_{11}O_4NCl]^{\cdot}Cl' + H_2O \rightarrow [C_{15}H_{11}O_4NCl]^{\cdot}OH' + HCl.$$
(V)

This base can be converted into a chloride or a bisulfate by reacting it with a 10% mineral acid solution, these salts being readily hydrolyzed by heating them carefully with water, thus regenerating the original base:

$$[C_{15}H_{11}O_4NCl]^{\cdot}OH' + HX \rightleftarrows H_2O + [C_{15}H_{11}O_4NCl]^{\cdot}X',$$
(VI)

where X = Cl, HSO_4.

The salts of the first and second intermediate products are isomers of each other. Physical and chemical properties are quite different, but they do possess a number of features in common. Thus the chlorine atoms in their molecules exhibit the same ability to oxidize an iodine ion to free iodine. They can be converted into the terminal betaine (III) or into its sulfur analog under the same conditions and with practically identical yields, while splitting out carbon dioxide and hydrogen chloride. The base $[C_{15}H_{11}O_4NCl]^{\cdot}OH'$ behaves similarly, yielding the betaine (III) with a yield of as high as 80%.

All these facts leave no room for doubt that the two intermediate products we isolated, which we identified as various salts, are actually the substances whose formation represents the intermediate stages of the transformation of the original triketone (I) into the terminal betaine (III). It is probable that the first of these intermediate products possesses the structure represented by Formula (V), while the second one is apparently an α-hydroxy acid (VI). It follows, therefore, that the mechanism involved in the hydrolytic cleavage of the ring system of the triketone (I), as well as the mechanisms underlying the secondary reactions that accompany this process, in no wise essentially differ from the analogous transformations previously discovered [3-10] in other carbocyclic compounds of similar structure.

EXPERIMENTAL*

1. Synthesis of 2-Chloro-2-pyridine-1,2,3,4-tetrahydronaphthalene-1,3,4-trione Chloride (I)

5.0 g of carefully desiccated 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine (II) was carefully ground to a fine powder and triturated with 30 ml of anhydrous chloroform. A stream of anhydrous chlorine was passed through the resultant mixture in a gentle, uniform flow for 3 hours, the mixture being cooled by cold water. The mixture soon began to turn light, while the precipitate became

*The analytical section of this research was carried out with the assistance of E. A. Ignatyeva, to whom we are deeply grateful.

viscous.

After an hour had elapsed, the substance became white; the particles that remained colored were retriturated. After the 3 hours were up, the white crystalline substance was suction filtered and repeatedly washed, at first with anhydrous chloroform and then with anhydrous ether. Drying at 15° and 5 mm to constant weight yielded 6.0 g (93%) of the triketone (I), a white, finely crystalline substance that turned yellow in storage; it darkens at 105° but does not fuse when heated to 250°. It is insoluble in organic solvents; it is readily soluble in water and aqueous alcohol, undergoing profound changes as it does so (vide infra).

Found %: N 4.05; Cl 21.97. $C_{15}H_9O_3NCl_2$. Computed %: N 4.34; Cl 22.05.
Determination of ionogenic chlorine. A weighed sample of the substance was dissolved in water and the chlorine was determined by the Volhard method. Found %: Cl' 10.84. $[C_{15}H_9O_3NCl]^+Cl'$. Computed %: Cl' 11.02.
Determination of oxidizing chlorine. A weighed sample of the substance was dissolved in 10 ml of alcohol, and 10 ml of concentrated hydrochloric acid plus 5 ml of a 1N aqueous solution of potassium iodide was added to the solution. The mixture was boiled for 15 minutes, cooled, and diluted with 100 ml of water, after which the iodine that separated out was titrated with a 0.1N solution of sodium hyposulfite. Number of atoms of oxidizing chlorine: 0.97.

2. Hydrolytic Cleavage of the Triketone (I)

a) In aqueous solution in the cold. The reaction was carried out at 19°. 1.0 g of the triketone (I) was added to 50 ml of water. The substance dissolved rapidly, and the solution turned yellow, the color growing deeper with time. After 10 hours had passed, the betaine (III) began to settle out of the solution as elongated yellow needles, which were filtered out three days later, washed with water, and desiccated at 105°. Weight: 0.322 g (47%).

Another 0.02 g was recovered after the filtrate had been boiled for 10 minutes. The overall yield of the betaine (III) was 50%. The substance was purified by double recrystallization from water to which activated charcoal had been added. M.p. 256-257°. (Vide infra for its properties).

b) By heating an aqueous solution. 1.0 g of the triketone (I) was dissolved in 20 ml of water. When the resultant solution was heated, carbon dioxide began to evolve, its evolution reaching a maximum at 95°, after which a yellow precipitate was thrown down almost instantaneously. The mixture was boiled for 20 minutes and then cooled; the precipitate was filtered out, washed with water, and recrystallized from hot water to which activated charcoal had been added. This yielded 0.384 g (55%) of the betaine (III). After the precipitate had been filtered out, the filtrate was divided into two halves. 20 ml of a 10% caustic soda solution was added to one half and about 20 ml of water was driven off from the mixture. The distillate was divided into two halves, one of which yielded pyridine in the form of its picrate (m.p. 163-164°); in the other half of the distillate, the pyridine was determined quantitatively, it being precipitated as the coordination compound $(CuPy_2)(CNS)_2$ with a solution of copper sulfate and then titrated with a solution of potassium thiocyanate. The excess of the latter was titrated back with a solution of silver nitrate [11]. Pyridine found: 0.0118 g. The total pyridine formed was 0.047 g (19%).

The second half of the filtrate was acidulated with sulfuric acid until the concentration of the latter in the solution reached 10%, after which it was exhaustively extracted with ether. The ether solution was desiccated with sodium sulfate, the ether was driven off, and the phthalic acid in the residue was determined by the method described in our Report II [12]. This yielded 0.0305 g of phthalic acid with a decomp. temp. of 198-200°. The phthalic acid formed totaled 0.061 g (12%).

c) In an alkaline medium. 1.0 g of the triketone (I) was dissolved in 20 ml of water and 5 ml of 1% caustic soda solution was added. The solution turned yellow-brown instantly, the odor of pyridine was noticed, and a precipitate of the betaine (III) was thrown down at once. Weight: 0.320 g (46%). The reactions with solutions of soda, ammonia, or sodium acetate were exactly the same.

The betaine (III) crystallizes from water or alcohol as elongated golden-yellow filaments. M.p. 256-257°. The substance is slightly soluble in ether, benzene, chloroform, and water; it is readily soluble in hot alcohol and hot acetone; it dissolves when heated in dilute acids and alkalies, settling out unchanged when the solution is cooled. It does not react with carbonyl-group reagents.

Found %: C 75.50; H 4.13; N 6.21; M 216 (cryoscopically in nitrobenzene). $C_{14}H_9O_2N$. Computed %: C 75.33; H 4.00; N 6.28; M 223.

Oxidation of the betaine (III) with potassium permanganate. 0.61 g of the substance was dissolved in 200 ml of water, and a 4% solution of potassium permanganate was added to the boiling solution a drop at a time until it was no longer decolorized. The excess permanganate was removed by adding alcohol, and – after the reaction mixture had been alkalinized – about 100 ml of water was driven off. Pyridine was determined in the distillate by the method specified in Experiment 2b. The pyridine yield was 0.1810 g (84%). The manganese dioxide was filtered out of the mixture left after the pyridine had been driven off, the filtrate was neutralized with sulfuric acid and evaporated to a small volume, and then the phthalic acid was determined by the method described in Report II [12]. This yielded 0.3580 g (79%) of phthalic acid with a m.p. of 200-201° (with decomposition).

d) Determination of the split out carbon dioxide and hydrogen sulfide. The apparatus used for this purpose was assembled as follows: a three-necked flask was connected to a gas tank filled with air by means of a tube, one end of which terminated at the top of the flask. Before entering the flask, the air was passed through a 20% alkali solution. The second flask opening was fitted with a reflux condenser, connected to two Tishchenko bottles containing a 20% alkali solution. A tube that slid freely in its stopper passed through the third neck of the flask. At the beginning of the test the end of the tube was at the top of the flask. This tube, fitted with a two-way stopcock, connected the three-necked flask to a two-necked one, extending to the bottom of the latter. The other opening of the two-necked flask was connected to a reflux condenser, the upper end of which was connected via a three-way stopcock to two Drexel bottles containing a titrated alkali solution. The system ended in a Tishchenko bottle that contained a 20% alkali solution.

100 ml of water was poured into the three-necked flask, the two-way stopcock was turned, connecting the three-necked flask to the rest of the apparatus, and the water was boiled for 30 minutes while a steady current of air was passed into the flask, the air being let out through the condenser, the opening of which was then closed. A weighed sample of the substance was placed in the two-necked flask, the two-way stopcock connecting the two flasks was opened, and air was passed through the two-necked flask for 30 minutes, being discharged via the three-way stopcock to the atmosphere. Finally, the tube connecting the two flasks was pushed down to the bottom of the three-necked flask, so that the air pressure forced water over into the two-necked flask. At the same time the exit of the air to the atmosphere was cut off by turning the three-way stopcock, the gasses being fed through the absorber system containing the titrated alkali solution. Then the reaction solution was boiled for 30 minutes, after which the alkali in the absorption bottles was titrated back with a 0.1 N acid solution, first against phenolphthalein and then against methyl orange.

Experimental results: Used 0.3335 g of the triketone (I). Consumed 8.22 ml of a 0.1N alkali solution, equivalent to 0.036 g of carbon dioxide. Yield of the latter: 80%: The precipitated betaine (III) was filtered out. Weight 0.085 g (37%). The amount of hydrogen chloride formed during the reaction was determined in the filtrate. We found 0.0656 g (87%) of HCl.

3. Reaction of the Triketone (I) With Potassium Iodide

30 ml of anhydrous acetone and 1.0 g of potassium iodide were added to 1.0 g of the triketone (I). The mixture was set aside to stand at room temperature, being agitated at periodic intervals. The solution darkened rapidly owing to the evolution of iodine. One hour later 20 ml of a 2% hyposulfite solution was added, and the acetone was driven off in the cold. The resultant precipitate was filtered out. This yielded 0.16 g (23%) of the betaine (III) with a m.p. of 255-257° (from water). After a few hours had elapsed, a yellow precipitate settled out of the filtrate; it fused at 289-290° after triple recrystallization from water to which activated charcoal had been added and exhibited no depression of the melting point when mixed with 2-pyridine-3(1)-oxy-1,4(3,4)-naphthoquinone betaine (II) [1]. Weight 0.10 g. Yield: 13%. After the betaine (II) had been removed, 5 ml of a 10% soda solution was added to the filtrate. A precipitate of the betaine (III) was thrown down almost at once. Weight: 0.24 g (35%). M.p. 255-257° (from water).

4. Conversion of the Triketone (I) into the Sulfur Analog of the Betaine (III)

5.0 g of the triketone (I) was mixed with 120 ml of anhydrous acetone and 4.0 g of potassium iodide. The mixture was set aside to stand for 2 hours at room temperature, being agitated periodically, after which 100 ml of a 2% hyposulfite solution was added, and the acetone was driven off in the cold. The solution was set aside to stand for 3-4 hours, after which the resultant precipitate, which constituted a mixture of the betaines (II) and (III) (Experiment 3), was filtered out. The filtrate was boiled for 20 minutes and then chilled, and the red substance formed was filtered out. The latter was washed with water, desiccated, carefully pulverized, and allowed to stand for several hours with 20 ml of carbon disulfide to remove the sulfur. This yielded 2.1 g (57%) of a sulfur analog of the betaine (III), which was twice recrystallized from alcohol to which activated charcoal had been added.* The compound consisted of bright-red rhombic crystals with a m.p. of 198-199°, which are very slightly soluble in water, but are soluble in methanol and ethyl alcohol, acetone, ether, and chloroform. This compound does not react with carbonyl-group reagents.

Found %: C 70.38; H 3.82; N 6.06. M 246, 239 (cryoscopically in nitrobenzene). $C_{14}H_8ONS$. Computed %: C 70.29; H 3.76; N 5.85; M 239

Conversion into the betaine (III). 1.2 g of the sulfur-containing substance was mixed with 2.5 g of lead acetate and 20 ml of alcohol. The mixture was boiled for 6 hours. The deposit gradually turned black, while the dark-red solution turned yellow. The mixture was filtered while hot, and the deposit washed on the filter paper with hot alcohol. The filtrates were combined, condensed to small volume, diluted with 50 ml of water, boiled with activated charcoal, and filtered. The betaine (III) settled out when the solution cooled Weight: 0.91 g (81%). M.p. 255-257° (from water).

5. Synthesis and Properties of the Chloride of the Compound (V)

1.0 g of the triketone (I) was placed in 15 ml of 10% hydrochloric acid. The substance dissolved rapidly, the solution turning pale yellow, and white prismatic crystals were thrown down almost instantly. The precipitate was filtered out,

*This compound was formed under the conditions described above owing to the presence of sodium tetrathionate in the solution.

washed several times with anhydrous acetone and then with anhydrous ether, and desiccated at 15° and 5 mm. This yielded 0.6 g (57%) of the chloride of the compound (V). The substance turns yellow in storage; it darkens at 100-105° but does not melt when heated up to 250°; it is insoluble in organic solvents, and readily soluble in water, though gradually undergoing profound changes as it does so (see below, Experiment 8). It dissolves in 10% hydrochloric acid when briefly heated, settling out unchanged when the solution cools.

Found %: C 53.14; H 2.95; N 4.43; Cl 20.66. $C_{15}H_{11}O_4NCl_2$. Computed %: C 52.94; H 3.23; N 4.12; Cl 20.85.

Determination of ionogenic chlorine (cf Experiment 1). Found %: Cl' 10.37. $[C_{15}H_{11}O_4NCl]^+Cl'$. Computed %: Cl' 10.43.

Determination of oxidizing chlorine (cf Experiment 1). Number of atoms of oxidizing chlorine: 1.02.

Conversion into the betaine (III). Using the same conditions as in Experiment 2a, we secured 50% of the betaine (III) with a m.p. of 255-257° (from water) at 19° in the course of 3 days, getting another 3% after 10 minutes of boiling. The overall yield was 53%. Using the conditions of Experiment 2b, we got 68% of the betaine (III), 11% of phthalic acid, and 19% of pyridine. Using the conditions of Experiment 2c, we secured a 51% yield of the betaine (III). The conditions of Experiment 2d yielded 50% of the betaine (III); the quantity of carbon dioxide split out was 93%, and that of hydrogen chloride 93.5%. All these substances were secured with practically the same yields when the last experiment was repeated without any atmospheric oxygen present.

Reaction with potassium iodide. 1.0 g of the chloride of Compound (V) was mixed with 30 ml of anhydrous acetone and 1.0 g of potassium iodide. The reaction conditions were the same as those in Experiment 3. But in this case the sole reaction product was the betaine (III), 0.18 g (27%) of which was formed after the acetone had been driven off and 0.34 g (52%) after treatment with soda. The overall yield of betaine (III) was 79%.

Conversion into the sulfur analog of the betaine (III). The reaction conditions were the same as those used for Experiment 4. We used 0.5 g of the chloride of the compound (V) for this reaction, securing 0.09 g (27%) of the betaine (III) and 0.20 g (57%) of its sulfur analog.

6. Preparation of the Nitrate of the Compound (V)

1.0 g of the triketone (I) was placed in 15 ml of 10% nitric acid. The substance dissolved rapidly, the solution turning pale yellow. A copious precipitate of the nitrate was thrown down almost instantly as colorless prisms. It was filtered out, washed with anhydrous acetone and then with anhydrous ether, and desiccated at 15° and 5 mm. This yielded 0.66 g (62%). The properties of the substance resembled those of the chloride described in Experiment 5.

Found %: N 7.63; Cl 9.56. $C_{15}H_{11}O_7N_2Cl$. Computed %: N 7.64; Cl 9.67.

Determination of the nitrate ion. A weighed sample of the substance was dissolved in water, and the resultant solution was heated for 30 minutes over a boiling water bath. The solution was cooled with ice water, and the precipitated betaine (III) was filtered out and washed with water until the reaction of the wash water was neutral. The latter was combined with the filtrate and heated over a boiling water bath, and the nitrate ion was precipitated with nitron. Found %: NO_3' 16.06. $[C_{15}H_{11}O_4NCl]^+NO_3'$. Computed %: NO_3' 16.92.

7. Preparation of the Bisulfate of the Compound (V)

1.0 g of the triketone (I) was dissolved in 15 ml of 10% sulfuric acid. White prisms of the bisulfate were precipitated almost immediately after the substance had dissolved. The precipitate was filtered out, washed with anhydrous

acetone and then with anhydrous ether, and desiccated at 15° and 5 mm. This yielded 0.75 g (60%) of a compound, the properties of which resembled those of the chloride and the nitrate described in Experiment 5 and 6.

Determination of the sulfate ion. A weighed sample of the substance was dissolved in water, and the sulfate ion was precipitated with barium chloride. Found %: SO_4'' 23.90. $[C_{15}H_{11}O_4NCl]^+HSO_4^-$. Computed %: SO_4'' 23.91.

Determination of the oxidizing chlorine (cf. Experiment 1). Number of atoms of oxidizing chlorine: 1.06.

8. Preparation of the Base of the Compound (VI)

This substance was prepared under identical conditions from the triketone (I) and from the chloride, nitrate, or sulfate of the compound (V), described in Experiments 1, 5, 6, and 7. 1.0 g of the substance was dissolved in 20 ml of water. Rubbing with a rod caused the precipitation of a copious cyrstalline deposit in the shape of lustrous, well-formed colorless rhombi. The synthesized compound was filtered out, washed with anhydrous acetone and then with anhydrous ether, and desiccated at 15° and 5 mm. The yield was about 75%. The substance changes much more quickly when stored than do the triketone (I) or the salts of the compound (V). Like the latter, it is insoluble in organic solvents. It darkens at 80-85°, but does not melt when heated up to 250°. It contains no ionogenic chlorine; the halogen contained in its molecule can oxidize potassium iodide to free iodine, though much less actively than in the case of the triketone (I) or the salts of the compound (V)

Found %: C 55.76; H 3.74; Cl 11.03. $[C_{15}H_{11}O_4NCl]^+OH^-$. Computed %: C 55.99; H 3.73; Cl 11.02.

Conversion into the betaine (III) and the latter's sulfur analog. The betaine (III) yield was 61% after 7 hours at 19° under the reaction conditions of Experiment 2a. The yield rose another 12% after 3 days, while another 7% of the betaine (III) could be secured by boiling the solution for 10 minutes. The overall yield was 80%. When this reaction was carried out under the conditions used for Experiment 2a, but with an equimolar quantity of hydrochloric acid present, the final yield as well as the rate of formation of the betaine (III) dropped (the yield was 56% after 3 days, an additional 9% being secured by boiling for 10 minutes; the overall yield was 65%). Using the conditions of Experiment 2b yielded: 72% of the betaine (III), 9% of phthalic acid, and 21% of pyridine. The conditions of Experiment 4 yielded 62% of the betaine (III) and 27% of the latter's sulfur analog.

9. Preparation of the Chloride of the Compound (VI)

1.0 g of the base described in Experiment 8 was placed in 15 ml of 10% hydrochloric acid. The substance dissolved rapidly with gentle heating, the chloride settling out as white needles almost all at once when the solution was cooled. The precipitate was filtered out, washed with anhydrous acetone and then with anhydrous ether, and desiccated at 15° and 5 mm. Weight: 0.90 g. Yield: 85%. The substance turns yellow in storage; it darkens at 115-120°, but does not melt when heated up to 250°. It is insoluble in organic solvents; it is readily soluble when gently heated in a small quantity of water, giving rise to the original base described in Experiment 8. It can be recrystallized from 10% hydrochloric acid. It contains 1 atom of ionogenic chlorine, the second chlorine atom being able to oxidize potassium iodide to free iodine.

Found %: Cl 20.87. $C_{15}H_{11}O_4NCl_2$. Computed %: Cl 20.85

Determination of ionogenic chlorine (cf Experiment 1). Found %: Cl' 10.65. $[C_{15}H_{11}O_4NCl]$·Cl'. Computed %: Cl' 10.42.

Conversion into the betaine (III) and the latter's sulfur analog. We secured 49% of the betaine (III) after 3 days at 19° under the conditions used in Experiment 2a, another 9% being secured after 10 minutes of boiling; the overall yield was 58%. The conditions of Experiment 2b yielded: 75% of the betaine (III), 8.5% of phthalic acid, and 21.5% of pyridine. The conditions of Experiment 4 yielded 27% of the betaine (III) and 57% of its sulfur analog.

10. Preparation of the Bisulfate of the Compound (VI)

1.0 g of the base described in Experiment 8 was placed in 15 ml of 10% sulfuric acid. The substance dissolved, the bisulfate settling out almost at once as white needles. The precipitate was filtered out, washed with anhydrous acetone and then with anhydrous ether, and desiccated at 15° and 5 mm. This yielded 0.92 g (74%) of a substance whose properties resembled those of the chloride described in Experiment 9.

Found %: N 3.44; Cl 8.53. $C_{15}H_{12}O_8NSCl$. Computed %: N 3.48; Cl 8.82. Determination of oxidizing chlorine (cf Experiment 1). Number of atoms of oxidizing chlorine: 1.04.

11. Rate of Conversion of the Triketone (I) and of the Intermediate Compounds (V) and (VI) into the Betaine (III)

1.0 g of the substance in question was dissolved in 50 ml of water, and the resultant solution was allowed to stand at a temperature of 19°. After the time specified in the table had elapsed, the precipitate of the betaine (III) was filtered out, the filtrate being allowed to stand at the same temperature. After 72 hours had passed, the filtrate was boiled for 10 minutes and the amount of precipitate formed was again determined. (See the table).

Substance	Per cent yield of the betaine (III)			
	At 19°, after			Overall yield after boiling for 10 minutes
	7 hours	24 hours	72 hours	
Triketone (I)	–	24	47	50
Chloride of the compound (V) ..	–	26	50	53
Base of the compound (VI)	61	–	73	80
Base of the compound (VI)**	–	23	56	65
Chloride of the compound (VI) .	–	24	49	58

SUMMARY

The chloride of 2-chloro-2-pyridine-1,2,3,4-tetrahydronaphthalene-1,3,4-trione has been synthesized and the conditions under which it is hydrolytically cleaved, as well as the nature of the cleavage, have been investigated. In addition, a study has been made of the mechanism of the secondary transformations that accompany the hydrolytic cleavage of this triketone.

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*** See CB translation p. 457 ff.

**** See CB translation p. p. 373 ff.

***** See CB translation p. 381 ff.

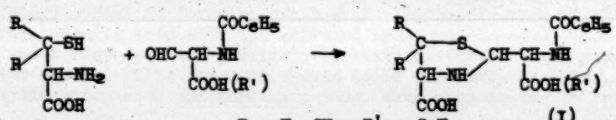
THE INTRODUCTION OF THE FORMYL RADICAL INTO AN ACYL AMINO ACID AND THE CONDENSATION OF THE RESULTING COMPOUNDS WITH THIOLAMINO ACIDS INTO THIAZOLIDINE DERIVATIVES

I. ETHYL FORMYLHIPPURATE AND ITS DERIVATIVES

A. S. Elina and O. Yu. Magidson

The objective of the present research has been the synthesis of some analogs of penicilloic acid, namely, α-(4-carboxy-2-thiazolidyl)-hippuric acid and α-(4-carboxy-5,5-dimethyl-2-thiazolidyl)-hippuric acid.

The shortest road to the synthesis of the foregoing compounds is the reaction of the respective thiolamino acids with formylhippuric acid or its ethyl ester.



R = H, CH_3; R' = C_2H_5. (I)

The simplest way to synthesize formylhippuric acid seemed to be formylating ethyl hippurate in a Claisen reaction. The only paper on the formylation of ethyl hippurate in the literature is one by Erlenmayer Jr. [1]. When we repeated this, we found that reacting hippuric ester with ethyl formate and sodium ethoxide in absolute alcohol yielded the sodium derivative of ethyl formylhippurate. But when we endeavored to isolate the ethyl formylhippurate and its sodium salt by the methods suggested by Erlenmeyer (acidulating an aqueous solution of the sodium salt of ethyl formylhippurate or adding the dry sodium salt to dilute hydrochloric acid), we were unable to recover an individual substance with a sharp melting point (just as Erlenmeyer was unable to). In both cases the ethyl formylhippurate was recovered either as an oily noncrystallizing substance or as a friable mass with a broad fusion temperature, extending over dozens of degrees, constituting a mixture of the carbonyl and enol forms of ethyl formylhippurate. The method of purifying ethyl formylhippurate described by Erlenmeyer involved allowing aqueous-alcoholic solutions of crude ethyl formylhippurate to stand for a long time at room temperature. When we resorted to the method of purifying ethyl formylhippurate recommended by Erlenmeyer, we secured an individual crystalline substance with a m.p. of 128°, which did not display the usual qualitative reactions for the presence of an aldehyde or oxymethylene group. Using the nonindividual and unpurified mixture as the initial substance for the ensuing reactions greatly lowered the yield of the reaction end products, so that we resolved to set about preparing pure ethyl formylhippurate.

We have found a way of isolating ethyl formylhippurate from its sodium salt in which the ethyl formylhippurate is immediately obtained in crystalline form.

This method involves the gradual addition of an aqueous solution of the sodium derivative of ethyl formylhippurate to a deeply chilled dilute solution of hydrochloric acid. The crystalline low-melting ethyl formylhippurate (m.p. 55-56°) thus produced consisted principally of the carbonyl form of ethyl formylhippurate with traces of the enol form. One, or sometimes two, precipitations of the resulting compound yielded the pure carbonyl form of ethyl formylhippurate, with a m.p. of 57-58°. It was identified by preparing its dinitrophenylhydrazone and its semicarbazone.

Crystalline ethyl formylhippurate that contains the enol form as an impurity tends to turn into an oily substance as the percentage of the enol form it contains rises. The less of the enol form there is in the ethyl formylhippurate, the slower is the shift toward an increase in the percentage of the enol form. Whereas the pure carbonyl form of ethyl formylhippurate was stored in crystalline form for a year and a half, exhibiting a $FeCl_3$ reaction only after it had been stored for six months, the crystalline ethyl formylhippurate that contained the enol form as an impurity "deliquesced" after standing for 2 weeks, its $FeCl_3$ reaction being much more intense. We were unable to secure pure formylhippuric acid by saponifying the ester group of ethyl formylhippurate with an alcoholic alkali. Despite the fact that the reaction was carried out at room temperature, all we got was hippuric acid instead of formylhippuric acid. We had to prepare the pure formylhippuric acid by a roundabout method. We converted the ethyl formylhippurate into its diethyl acetal. The ester group of the ethyl formylhippurate diethyl acetal was saponified with an alcoholic alkali, the reaction yielding the diethyl acetal of formylhippuric acid. Saponification of the diethyl acetal of formylhippuric acid with concentrated hydrochloric acid yielded formylhippuric acid, which displayed the qualitative reactions for both the oxymethylene and aldehyde groups. This compound proved to be extremely unstable, losing its carboxylic group with extraordinary ease, even when heated in low-boiling solvents.

In view of the instability of formylhippuric acid, we employed the diethyl acetal of formylhippuric acid instead of the acid itself in our synthesis of α-(4-carboxy-2-thiazolidyl)-hippuric acid. A study of the condensation of l-cysteine hydrochloride with the diethyl acetal of formylhippuric acid indicated that when mild conditions were employed (organic solvent, room temperature), the thiazolidine ring was not formed, apparently because of the comparatively high stability of the acetal group of the diethyl acetal of formylhippuric acid. When the conditions used were more severe (aqueous medium, temperatures ranging up to 90°), the reaction resulted in formation of the thiazolidine ring, but also caused the labile carboxyl group to split off. Instead of the expected analog of penicilloic acid we got 2-benzoylaminomethyl-4-carboxythiazolidine.

It was much easier to prepare the thiazolidine derivative by reacting the formyl-hippuric ester with l-cysteine hydrochloride. Here cyclization occurred at room temperature in methanol, the reaction resulting in the formation of the ethyl ester of α-(4-carboxy-2-thiazolidyl)-hippuric acid.

We synthesized the ethyl ester of α-(4-carboxy-5,5-dimethyl-2-thiazolidyl)-hippuric acid by reacting d,l-dimethylcysteine (hydrobromide or hydrochloride*) with ethyl formylhippurate at 50-60° without any solvent.

The synthesis of 2-phenyl-4-ethoxymethyleneoxasolinone-(5) was an offshoot of our principal objective; this compound had acquired considerable interest after the publication of the paper by du Vigneaud and his associates [2] on the synthesis of penicillin, as an analog of one of the components used by du Vigneaud to synthesize penicillin. We synthesized 2-phenyl-4-ethoxymethyleneoxazolinone-(5)

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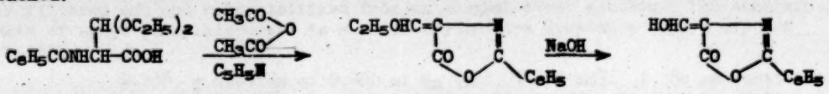
* The d,l-dimethylcysteine was synthesized in the All-Union Research Institute of Pharmaceutical Chemistry.

by heating the diethyl acetal of formylhippuric acid for half an hour with acetic anhydride and pyridine; an azlactone ring was formed, while one ethoxy group was detached.



Treating 2-phenyl-4-ethoxymethyleneoxazolinone-(5) with a 5% solution of NaOH at room temperature saponified the ethoxy group, yielding 2-phenyl-4-oxymethyleneoxazolinone-(5).

EXPERIMENTAL

Formylation of ethyl hippurate. 5.8 g of metallic sodium was gradually added to 90 ml of absolute alcohol. 19 g of ethyl formate was then added to the solution of sodium ethoxide, with chilling and constant stirring. Two hours later 50 g of ethyl hippurate was gradually added to the reaction mixture. The reaction temperature was 12-16°. The reaction mass was stirred for two more hours after the ethyl hippurate had been added, after which the flask was stoppered and set aside to stand for 15 days. After this period had elapsed, the sodium derivative of ethylformylhippurate was filtered out, carefully washed with absolute alcohol, and desiccated. This yielded 46.5 g of the sodium derivative of ethyl formylhippurate.

Isolation of the keto form of ethyl formylhippurate. 10 g of the dry sodium derivative of ethyl formylhippurate was dissolved in 40 ml of water. The solution was treated with activated charcoal and filtered. The filtrate was gradually added, with constant stirring and chilling, to 48 ml of 7% hydrochloric acid. The oily substance that formed at first quickly began to crystallize. The reaction mass was kept at low temperature for several hours to effect complete precipitation. The formylhippurate was filtered out, washed with ice water, and dried in a vacuum desiccator. This yielded 7 g of ethyl formylhippurate, an alcoholic solution of which still displayed faint coloring with $FeCl_3$; m.p. 52-54°. The 7 g of formylhippurate was dissolved in 40 ml of chilled 4% NaOH solution. The solution was treated with charcoal and filtered, the filtrate being gradually added to 30 ml of chilled 7% hydrochloric acid. This yielded a crystalline substance, which was filtered out, washed with ice water, and dried in a vacuum-desiccator. The yield was 5.5 g; m.p. 57-58°. When $FeCl_3$ was added to alcoholic solutions, no coloring resulted. The colorless crystals are freely soluble in alcohol, less so in ether; they are soluble when heated in chloroform or benzene.

11.762 mg substance: 5.03 ml 0.01 N H_2SO_4. Found %: N 5.99.
$C_{12}H_{13}O_4N$. Computed %: N 5.95.

Dinitrophenylhydrazone of ethyl formylhippurate. 0.6 g of ethyl formylhippurate was dissolved in 80% ethyl alcohol. A saturated alcoholic solution of 0.6 g of dinitrophenylhydrazine and a drop of concentrated hydrochloric acid was added to the solution. The solution was then gently heated over a water bath for five minutes. The dinitrophenylhydrazone of ethyl formylhippurate that settled out as a bright-yellow crystalline precipitate was filtered out and crystallized repeatedly from alcohol: m.p. 178-179°.

3.812 mg substance: 0.580 ml N_2 (22°, 735 mm). Found %: N 17.04.
$C_{18}H_{17}O_7N_5$. Computed %: N 16.86.

Semicarbazone of ethyl formylhippurate. 0.8 g of ethyl formylhippurate and 0.5 g of semicarbazide were dissolved in a mixture of 16 ml of water and 10 ml of ethyl alcohol. 0.5 g of sodium acetate was added to the reaction solution. Two hours later, the semicarbazone began to settle out. The reaction mass was

allowed to stand at room temperature for 36 hours. The crystalline semicarbazone was filtered out and recrystallized from an alcohol-ether mixture. The semicarbazone of ethyl formylhippurate is a white crystalline substance with a m.p. of 164-165°.

2.736 g substance: 0.460 ml N_2 (18°, 746.5 mm). 2.784 mg substance: 0.476 ml N_2 (19.5°, 746 mm). Found %: N 19.39, 19.59. $C_{13}H_{16}O_4N_4$. Computed %: N 19.18.

Detaching the formyl group from ethyl formylhippurate. 3 g of ethyl formylhippurate was placed in a solution of 1.2 g of NaOH in 20 ml of 80% ethyl alcohol. The reaction solution was set aside to stand overnight. The alcohol was driven off in vacuum at 25-30°. The residue was dissolved in water, treated with activated charcoal, and – while deeply chilled – acidulated with hydrochloric acid until its reaction was slightly acid with Congo red. This yielded 2.1 g of hippuric acid (m.p. 185-187°); exhibited no depression of the melting point when mixed with known hippuric acid.

Acetal of ethylformylhippurate. 5.3 g of ethyl formylhippurate was dissolved in 50 ml of absolute ethyl alcohol, in which 0.5 g of anhydrous HCl had previosly been dissolved. The solution was boiled for 5.5 hours, after which the alcohol was driven off in vacuum. The residue, an oily substance, was dissolved in ether, and the ether solution was carefully washed with a 10% solution of K_2CO_3. The ether solution was then desiccated with calcined K_2CO_3, and the ether was driven off. There remained 5 g of the acetal of ethyl formylhippurate – a thick yellow oil with a b.p. of 145-150° at 0.25 mm residual pressure, or 169-170° at 1 mm residual pressure.

9.858 mg substance: 0.426 ml N_2 (25°, 736.4 mm). 9.490 mg substance: 0.414 ml N_2 (28.5°, 730.4 mm). 5.325 mg substance: 15.19 ml 0.05 N $Na_2S_2O_3$. Found %: OC_2H_5 42.82; N 4.8, 4.74. $C_{16}H_{23}O_5N$. Computed %: OC_2H_5 43.69; N 4.53.

Acetal of formylhippuric acid. 5 g of the acetal of ethyl formylhippurate was dissolved in 40 ml of ethyl alcohol. 2.2 ml of NaOH (sp. gr. 1.457) was added to the solution, which was then allowed to stand for 48 hours. After this period had elapsed, the alcohol was driven off in vacuum at 30-35°. The crystalline residue was dissolved in water, treated with charcoal, and filtered. The filtrate was deeply chilled and then acidulated with dilute (1:3) HCl until its reaction was slightly acid with Congo red, and the acetal of formylhippuric acid that settled out was then and there extracted with ether. The ether solution was washed 2 or 3 times with water and desiccated with anhydrous Na_2SO_4, after which the ether was driven off. The residue was an oil, which crystallized upon standing – weight: 3.8 g. After recrystallization from a mixture of benzene and petroleum ether the acetal of formulhippuric acid consisted of colorless needles with a m.p. of 88-89°, which were soluble in bicarbonate, alcohol, ether, and benzene, and insoluble in petroleum ether.

8.016 mg substance: 0.357 ml N_2 (21°, 737.6 mm). 8.758 mg substance: 0.392 ml N_2 (21.5°, 737.2 mm). Found %: N 5.01, 5.03. $C_{14}H_{19}O_5N$. Computed %: N 4.98.

Formylhippuric acid. 1 g of the acetal of formylhippuric acid was treated with 5 ml of 20% hydrochloric acid at room temperature. At first nearly all of it dissolved. Crystallization set in after a few minutes had elapsed. The precipitate was filtered out after two hours had passed. This yielded 0.6 g of formylhippuric acid. After recrystallization from dichloroethane, formylhippuric acid consists of colorless lustrous crystals, which are soluble in bicarbonate, form a silver mirror, and color $FeCl_3$ slightly. The melting point of formylhippuric acid is 86-87° (close to the melting point of the acetal of formylhippuric acid). A test sample of formylhippuric acid, mixed with the acetal of formylhippuric

acid, fused at 74-76°.

7.370 mg substance: 0.453 ml N_2 (23.5°, 747 mm). Found %: N 6.96. $C_{10}H_9O_4N$. Computed %: N 6.76.

2-Benzoylaminomethyl-4-carboxythiazolidine. 0.4 g of the diethyl acetal of formylhippuric acid was mixed with 0.22 g of l-cysteine hydrochloride. 0.5 ml of water was added to the mixture, and the reaction mass was heated over a boiling water bath for a few minutes until the solution became transparent. Gas was evolved during the course of the reaction. The resulting solution was poured into water and 0.1 g of $NaHCO_3$ was added to neutralize it. A total of 0.35 g of the colorless crystalline precipitate of 2-benzoylaminomethyl-4-carboxythiazolidine was secured. The 2-benzoylaminomethyl-4-carboxythiazolidine fused at 173-174° after recrystallization from 70% ethyl alcohol.

8.206 mg substance: 6.08 ml 0.1N H_2SO_4. 6.672 mg substance: 5.995 mg $BaSO_4$. Found %: N 10.37; S 12.34. $C_{12}H_{14}O_3N_2S$. Computed %: N 10.52; S 12.05.

Ethyl α-(4-Carboxy-2-thiazolidyl)hippurate. A solution of 2.7 g of l-cysteine hydrochloride in 15 ml of methanol was mixed with 4.7 g of ethyl formylhippurate dissolved in 15 ml of methanol. The reaction proceeded at room temperature. Forty eight hours later the precipitated ethyl α-(4-carboxy-2-thiazolidyl)hippurate, totalling 3 g, i.e., 50.8% of the theoretical quantity, was filtered out. The ethyl-α-(4-carboxy-2-thiazolidyl)hippurate consisted of colorless smooth needles with a m.p. of 160-161° after crystallization from 80% methanol, which are insoluble in water, difficultly soluble in benzene and chloroform, and freely soluble in alcohol.

6.931 mg substance: 4.00 ml 0.01N NaOH. 7.400 mg substance: 4.21 ml 0.01N NaOH. 7.224 mg substance: 4.871 mg $BaSO_4$. Found %: N 8.12, 8.01; S 9.26. $C_{15}H_{18}O_5N_2S$. Computed %: N 8.28; S 9.47.

Hydrobromide of ethyl α-(4-carboxy-5,5-dimethyl-2-thiazolidyl)-hippurate. 2 g of ethyl formylhippurate was triturated with 1.6 g of d,l-dimethylcysteine hydrobromide. The mixture was heated for 3.5-4 hours at a bath temperature of 50-60° until a sample of the reaction mass no longer was colored when reacted with sodium nitroprusside. After the reaction was over, the melt was ground to a powder and crystallized from a mixture of ether and methanol. This yielded 1.5 g of the hydrobromide of ethyl α-(4-carboxy-5,5-dimethyl-2-thiazolidyl)-hippurate. The mother liquor yielded another 0.6 g of this compound. The hydrobromide of ethyl α-(4-carboxy-5,5-dimethyl-2-thiazolidyl)-hippurate is a colorless crystalline substance with a m.p. of 173-174° (with decomposition), which is rather freely soluble in water (the hydrobromide is hydrolyzed when the aqueous solution is allowed to stand), insoluble in ether, and freely soluble in methanol and ethyl alcohol.

0.144 g substance: 0.0733 g $BaSO_4$. 9.953 mg substance: 4.42 ml 0.01N H_2SO_4. 10.104 mg substance: 4.43 ml 0.01N H_2SO_4. 7.985 mg substance: 3.295 mg AgBr. Found %: S 6.97; N 6.22, 6.14; Br 17.57. $C_{17}H_{22}O_5N_2S \cdot HBr$. Computed %: S 7.16; N 6.26; Br 17.87.

2-Phenyl-4-ethoxymethyleneoxazolinone-(5). A solution of 1.45 g of the diethyl acetal of formylhippuric acid in 7 ml of acetic anhydride was heated with 0.9 g of anhydrous pyridine over a water bath for half an hour. The acetic anhydride and the pyridine were driven off in vacuum. This left behind 0.8 g of crystalline 2-phenyl-4-ethoxymethyleneoxazolinone-(5). After recrystallization from petroleum ether the 2-phenyl-4-ethoxy-methyleneoxazolinone-(5) consisted of colorless needles with a m.p. of 95-96°, which are insoluble in bicarbonate, freely soluble in acetic anhydride and benzene, and somewhat less so in ethyl alcohol and petroleum ether. It decolorizes $KMnO_4$ instantaneously in a Na_2CO_3 solution.

8.026 mg substance: 11.14 ml 0.02N $Na_2S_2O_3$. 7.840 mg substance: 3.68 ml 0.01N H_2SO_4. 7.998 mg substance: 3.73 ml 0.01N H_2SO_4. Found %: OC_2H_5 20.83; N 6.57, 6.53. $C_{12}H_{11}O_3N$. Computed %: OC_2H_5 20.74; N 6.45.

SUMMARY

1. A study has been made of the formylation of ethyl hippurate, and the carbonyl form of ethyl hippurate has been isolated; the latter was identified by its semicarbazone and dinitrophenylhydrazone.

2. Formylhippuric acid has been synthesized by preparing the diethyl acetal of ethyl formylhippurate and saponifying first the ester group and then the diethyl acetal group.

3. It has been found that condensing the diethyl acetal of formylhippuric acid with l-cysteine hydrochloride at 90° in an aqueous medium closes the thiazolidine ring, detaches a carboxyl group, and gives rise to 2-benzoylaminomethyl-4-carboxythiazolidine.

4. The ethyl esters of α-(4-carboxy-2-thiazolidyl)- and α-(4-carboxy-5,5-dimethyl-2-thiazolidyl)-hippurates have been synthesized by reacting ethyl formylhippurate with l-cysteine and d,l-dimethylcysteine, respectively (using their hydrochlorides or hydrobromides).

5. 2-Phenyl-4-ethoxymethyleneoxazolinone-(5)-has been synthesized by heating the diethyl acetal of formylhippuric acid with acetic anhydride and pyridine.

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POLAROGRAPHIC INVESTIGATION OF SULFAMIDE COMPOUNDS

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INTRODUCTION

During the past few years numerous sulfamide compounds have been widely employed as therapeutic preparations. Their successful use in curing disease was closely bound up with therapeutic and biological researches. Subsequent investigation of the interrelationships between molecular structure and curative action made it possible to plan the synthesis of a series of new compounds with more farreaching specific actions. These researches were paralled by studies of the physical and chemical properties of sulfamide compounds, while methods were elaborated for their qualitative and quantitative determination.

In the present research we have investigated the reduction of several sulfamide derivatives at a mercury dropping electrode. We were interested in establishing the relationship between the composition of the molecule of a sulfamide compound and the latter's ability to be reduced at the mercury drop and to yield a diffusion current at a certain potential of the mercury dropping electrode.

EXPERIMENTAL

We prepared aqueous or alcoholic solutions of the sulfamide preparations of known concentration for these experiments, adding them to the background solution in the electrolyzer. It was found that only solutions of tetrasubstituted bases could be employed as indifferent electrolytes. It was impossible to use acid solutions for polarography, since the reduction potentials of sulfamide preparations are, as a rule, highly negative potentials of the dropping electrode. Measurements were made with no air present, in an atmosphere of hydrogen, at 25 ± 0.3°. The polarograph readings were made visually.

a) Sulfanilamide (white streptocide $NH_2C_6H_4SO_2NH_2$). This sulfamide preparation is not reduced at a dropping mercury electrode. We were unable to secure diffusion currents of the white streptocide up to the potential of the mercury dropping electrode, -2.3 volts, that corresponded to the reduction of the background solution of tetramethyl-ammonium iodide.

b) Albucide (N-acetylsulfanilamide, $NH_2C_6H_4SO_2NHCOCH_3$). Albucide is rather freely soluble in water, so that we used aqueous solutions in our research. No diffusion currents were found where we used 1N solutions of caustic soda and lithium chloride. Only when we used a 0.1N solution of tetramethylammonium iodide were we able to observe clearly marked diffusion currents on the polarogram. The numerical values of the diffusion current and the half-wave potentials of albucide at various concentrations of the latter are given in Table 1.

The polarograms of the albucide waves are given in Fig. 1. There is a linear relationship between the diffusion current and the concentration of albucide. The graduated straight line is shown in Fig. 2. It should be noted that when albucide solutions with concentrations higher than 2.10^{-2} mol/liter were examined in the polarograph, the polarization curves exhibited maxima; gelatin can be used to suppress these latter.

TABLE 1

Diffusion Currents and Half-Wave Potentials of Albucide Referred to a Saturated Calomel Electrode

Concentration, (mol/liter)·10^3	Current, microamperes	Half-wave potential, volts
2.3	3.6	-2.16
3.6	6.6	-2.16
4.5	7.4	-2.16
7.2	12.3	-2.18
13.4	21.3	-2.20

Fig. 1. Polarograms of the waves of albucide.

1-Background solution 0.1N $(CH_3)_4NI$; 2-albucide concentration $2.3 \cdot 10^{-3}$ mol/liter; 3-$3.6 \cdot 10^{-3}$ mol/liter; 4-$4.5 \cdot 10^{-3}$ mol/liter; 5-$7.2 \cdot 10^{-3}$ mol/liter; 6-$13.4 \cdot 10^{-3}$ mol/liter.

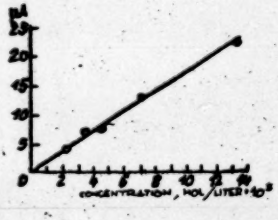
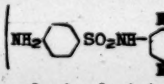
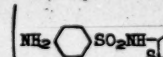


Fig. 2. Graduated straight line to determine albucide in a background solution of 0.1N $(CH_3)_4NI$.

c) Sulfidine . Sulfidine is only very slightly soluble in water or in alcohols, which makes polarograph study and the recording of good waves extremely difficult. Our research has shown that sulfadine is reduced at about -1.8 volts referred to a saturated calomel electrode when 0.5N tetramethylammonium iodide is present. The polarograms must be recorded with all air excluded.

d) Sulfadiazine  . Sulfadiazine is reduced at potentials of the mercury dropping electrode totaling some -1.8 volts in a background solution of 0.1N tetramethylammonium iodide. Since the reduction currents are extremely small, apparently owing to the extremely low solubility of sulfadiazine, the securing of reproducible results meets with some difficulty.

e) Sulfathiazole  . The polarograms of sulfathiazole were plotted in aqueous solutions of methanol containing about 10% of the latter. When we used 0.1N solutions of hydrochloric acid, calcium chloride, potassium nitrate, and lithium chloride, or a 2N solution of caustic soda as the background solution, the sulfathiazole was not reduced. Clearly marked waves were secured when the background solution used was a 0.1N solution of a salt of a tetrasubstituted base. The diffusion currents and half-wave potentials are given in Table 2.

The sulfathiazole current is directly proportional to the concentration (Fig. 4, straight line A).

TABLE 2

Diffusion currents and Half-Wave Potentials of Sulfathiazole Referred to a Saturated Calomel Electrode

Concentration, (mol/liter)·10^3	Current, microamperes	Half-wave potential, volts
2.04	0.38	-1.66
3.92	1.035	-1.69
5.85	1.50	-1.68
7.45	2.26	-1.70
9.0	2.82	-1.68
10.4	3.29	-1.74
11.7	3.95	-1.72
14.7	4.89	-1.74

TABLE 3

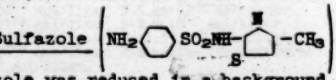
Diffusion Currents and Half-Wave Potentials of Sulfazole Referred to a Saturated Calomel Electrode

Concentration, (mol/liter)·10^3	Current, microamperes	Half-wave potential, volts
1.4	0.38	-1.73
2.1	1.21	-1.65
2.7	1.98	-1.68
4.0	4.5	-1.66
4.5	5.45	-1.66

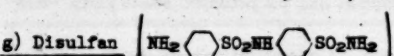
TABLE 4

Diffusion Currents and Half-Wave Potentials of Disulfan Referred to a Saturated Calomel Electrode

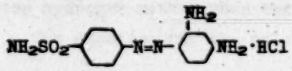
Concentration, (mol/liter)·10^3	Current, microamperes	Half-wave potential, volts
2.05	1.03	-1.70
3.10	1.78	-1.74
4.20	2.35	-1.76
4.80	3.02	-1.80
7.9	4.42	-1.86

f) Sulfazole 

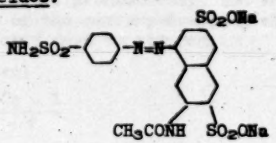
Sulfazole was reduced in a background solution of 0.1N tetramethylammonium-iodide. The diffusion currents are readily reproducible and may be employed for quantitative analysis. Table 3 gives the numerical values of the diffusion currents of sulfazole and the half-wave potentials for various concentrations of this sulfamide preparation. The polarograms of sulfazole exhibit maxima that cannot be suppressed with gelatin. The diffusion current is directly proportional to the concentration of sulfazole only at concentrations ranging from $1.5 \cdot 10^{-3}$ mol per liter to $4.5 \cdot 10^{-3}$ mol/liter. At lower sulfazole concentrations the sulfazole wave is so small as to be reliably measured only with great difficulty. The solution is saturated at a sulfazole concentration of $5 \cdot 10^{-3}$, so that the current rises no higher.

g) Disulfan  . Disulfan was reduced at the mercury dropping electrode in the presence of a 0.1N solution of a salt of a tetrasubstituted base. The currents are readily reproducible and may be used in quantitative determinations (Fig. 3, Curve 2). Table 4 gives the currents and the half-wave potentials of disulfan at various concentrations of the latter. The current is directly proportional to the concentration, provided the percentage of disulfan in the solution is not too high and the solution is not yet saturated. The graduated straight line for disulfan is given in Fig. 4 (Line B).

h) Basic (I) and Soluble (II) Streptocides.



(I)



(II)

Like sulfanilamide (white streptocide), the basic (I) and soluble (II) streptocides do not exhibit diffusion currents under the conditions employed in our investigation and, hence, come under the heading of unreducible substances.

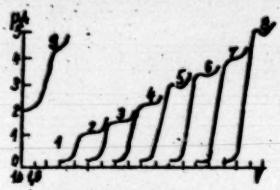


Fig. 3. Polarograms of the waves of sulfathiazole and disulfan in a solution of 0.1N $(CH_3)_4NI$.

1-Sulfathiazole concentration $2.04 \cdot 10^{-3}$ mol/liter; 2-$3.92 \cdot 10^{-3}$ mol/liter; 3-$5.85 \cdot 10^{-3}$ mol/liter; 4-$7.45 \cdot 10^{-3}$ mol/liter; 5-$9.0 \cdot 10^{-3}$ mol/liter; 6-$10.4 \cdot 10^{-3}$ mol/liter; 7-$11.7 \cdot 10^{-3}$ mol/liter; 8-$14.7 \cdot 10^{-3}$ mol/liter; 9-disulfan concentration $4.2 \cdot 10^{-3}$ mol/liter.

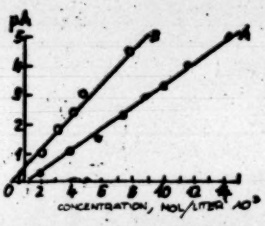


Fig. 4. Graduated straight lines for determining sulfathiazole (A) and disulfan (B) in a 0.1N $(CH_3)_4NI$ solution.

EVALUATION OF RESULTS

Our researches indicate that not all sulfamide compounds are reduced at the mercury dropping electrode. Thus, sulfanilamide exhibits no diffusion currents, whereas sulfamide derivatives that contain heterocyclic rings, such as sulfathiazole, sulfazole, etc., are reduced.

The absence of reducibility in the basic streptocide and the soluble streptocide is rather unexpected. We know of several instances where molecules that contain $-N=N-$ groups are reduced at the mercury dropping electrode. The presence of the $-\underset{\underset{}{}}{\overset{\overset{H}{|}}{N}}-\overset{\overset{O}{\|}}{C}-CH_3$ group in the molecule of the soluble streptocide does not enable this compound to be reduced at the mercury cathode, possibly because it is converted into a group with a different electron arrangement $-\overset{\overset{H}{|}}{N}=\overset{\overset{O}{\|}}{C}-CH_3$ (+ on N, − on O). The same factor probably stabilizes the albucide molecule pronouncedly, the latter being reduced only at highly negative potentials of the mercury dropping electrode, it being hydrogen rather than the molecule itself that is reduced.

The equation for the polarographic wave:

$$\pi = \pi_{1/2} + \frac{2.3RT}{nF} \log \frac{i_d - i}{i}$$

holds good for all the compounds we have investigated, provided there are no

maxima on the polarization curve.

The slope of the straight line when plotted in $\pi - \log \frac{i_d - i}{i}$ coordinates gives a value slightly higher than 0.5 for n, the number of electrons taking part in reduction. It is probable that this fractional value of n may be due to the irreversible reduction process and the complexity of the reactions occurring at the electrode. We used the experimental data to compute the diffusion coefficients of the molecules of those sulfamides that are reduced at the mercury dropping electrode. We used Ilkovich's equation:

$$i_d = 605nD^{1/2}m^{2/3}t^{1/6}C,$$

in these calculations, n being assumed to equal 1. The diffusion coefficient was found to be extremely low for all the molecules - of the order of 10^{-7} to 10^{-8}. The highest value found applied to albucide: $0.28 \cdot 10^{-5}$ cm^2/sec.

It is quite possible that hydrogen may be reduced in the series of examples we have considered. Sulfamide derivatives possess extremely weak acidic properties, so that the concentration of hydrogen ions does not correspond to the concentration of the sulfamide, but is merely a small fraction of the latter. In polarography, as we know, the reduction potential shifts to more highly negative values when weak acids are reduced in an excess of an indifferent electrolyte. This may be the case with disulfan, sulfathiazole, and others, for whom the measured diffusion coefficients possess the smallest numerical values. These same compounds have reduction potentials that are in close proximity to one another, even though their molecules are quite different.

It should be noted that the polarographic method of analysis may be employed for the quantitative determination of disulfan, sulfathiazole, albucide, sulfazole, sulfadiazine, and others. The best results will be obtained if solutions containing salts of tetrasubstituted bases are used as a background.

SUMMARY

1. A study has been made of the reduction of several sulfamide derivatives at the mercury dropping electrode. It has been found that albucide, sulfathiazole, sulfazole, sulfadiazine, and sulfidine can be reduced and exhibit a diffusion current in solutions that contain as background a 0.1N solution of tetramethylammonium iodide.

2. Of the sulfamides, those compounds are reduced that possess reducible atom groups or are weak acids. The basic and the soluble streptocides are not reduced at the mercury dropping electrode.

3. The reduction of several sulfamide derivatives conforms to the equation of a polarographic wave. The calculated diffusion coefficients are extremely small.

4. The polarographic method of analysis may be employed for the quantitative determination of some sulfamide preparations.

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THE SYNTHESIS OF THE DIMETHYLAMINOETHYL ESTER OF DIPHENYLCARBINOL (BENADRYL) AND ITS ANALOGS

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The dimethylaminoethyl ester of diphenylcarbinol (benadryl) is one of the most active of the antihistamines, possessing a number of valuable physiological properties in addition to its negligible toxicity: it reduces spasms of the smooth muscles 650 times as strongly as papaverine; it relieves the constriction of the bronchi caused by histamine 15 to 30 times as strongly as aminophyllin; and it counteracts the vascular dilating action of histamine. We also possess reports on the anesthetic action of the dimethylaminoethyl ester of diphenylcarbinol (benadryl) [1]. This compound has been synthesized by condensing diphenylbromomethane with dimethylaminoethanol [2].

We have synthesized the dimethylaminoethyl ester of diphenylcarbinol and of its analogs by heating diphenylcarbinol and benzyl alcohol with the respective amino alkyl chlorides over a water bath in the presence of an alcoholic solution of a sodium alcoholate. The reaction was carried out with the hydrochlorides as well as with the bases of amino alkyl chlorides. The best results are obtained by using the bases. Bases that have been freshly prepared from their salts must be used in these condensations, for these bases polymerize extremely easily upon standing or upon heating, forming solid cyclic dimers [3]. This is the reason for the lower yields of the amino esters and the recovery of the unreacted components. Dimethylaminoethyl chloride was synthesized by the method we have described previously. Diethylaminopropyl chloride was prepared by reacting trimethylene chlorobromide with diethylamine hydrochloride in the presence of an excess of a 40% solution of caustic soda. Dimethylaminopropyl chloride was synthesized analogously by heating it over a water bath in sealed tubes or by letting it stand at room temperature for 2 to 3 days. All these amino alkyl chlorides were secured as their hydrochlorides and were converted into bases only at the time of their condensation with diphenylcarbinol and benzyl alcohol.

$(C_6H_5)_2CHOR$ (I) $C_6H_5CH_2OR$ (II)

$R = -CH_2CH_2N(CH_3)_2$, $-CH_2CH_2CH_2N(C_2H_5)_2$, $-CH_2CH_2CH_2N(CH_3)_2$.

EXPERIMENTAL

1. Diethylaminopropyl chloride. This was prepared by heating to 36°, with constant stirring, a mixture of 15 g (1.0 mol) of diethylamine, 48 g (1.5 mols) of trimethylene chlorobromide and 20 g of a 40% solution of caustic soda, followed by heating the reaction mixture to 38-40° for 6-7 hours. After the reaction was over,

* Deceased.

water was added to dissolve the sodium bromide formed. The oily layer was separated and acidulated with 3-5 ml of hydrochloric acid (sp. gr. 1.17) to convert the unreacted diethylamine into a hydrochloride; the excess trimethylene chlorobromide and the resulting diethylaminopropyl chloride were isolated as an oil, which was treated with an excess of hydrochloric acid, the trimethylene chlorobromide being extracted with ether. The aqueous solution was evaporated in ether. This yielded 20-23 g (some 68%) of the crystalline hydrochloride of diethylaminopropyl chloride. The base was isolated by reacting a concentrated solution of the salt with potash. B.p. 165-166°.

2. Dimethylaminopropyl chloride. This was prepared from 15.4 g (1.1 mols) of trimethylene chlorobromide, 13 g (1.0 mol) of a 33% aqueous solution of dimethylamine, and 4 g of a 40% caustic soda solution by allowing the mixture to stand at 12-14° for 2 to 3 days. The resultant oil, which contains the original constituents and the resultant dimethylaminopropyl chloride, was extracted with ether. The dimethylamine was driven off together with the solvent, the residue being acidulated with dilute hydrochloric acid and the trimethylene chlorobromide being extracted with ether. The aqueous solution was evaporated to dryness in vacuum. The hydrochloride of dimethylaminopropyl chloride was recovered as strongly hygroscopic crystals that deliquesce in air. Yield: 7.8 g (52% of the theoretical). The base was secured by reacting a concentrated aqueous solution of the salt with a 50% solution of caustic potash. M.p. 134-135° [4].

3. Dimethylaminoethyl ester of diphenylcarbinol. An alcoholic solution of sodium ethylate, prepared from 0.5 g of sodium and 12 ml of absolute alcohol, was heated for 20-30 minutes with 4 g of diphenylcarbinol over a water bath. 2.5 g of dimethylaminoethyl chloride was gradually added to the hot solution, after which heating was continued for 6 hours. The reaction mass was diluted with water until the precipitated sodium chloride dissolved, then acidulated with hydrochloric acid, and the unreacted diphenylcarbinol was extracted with ether. The aqueous solution was treated with potash, carefully extracted with ether, and desiccated over potash. The oil left after the ether had been driven off was distilled in vacuum. The excess dimethylaminoethyl chloride was driven off at 9 mm and 20-22°, and the dimethylaminoethyl ester of diphenylcarbinol was distilled at 172-174° as a light-yellow oil that is freely soluble in organic solvents, though insoluble in water. The yield was 1 g (18% of the theoretical), though the yield was 40% of the theoretical if allowance is made for the regenerated diphenylcarbinol.

d_{28}^{28} 1.020; n_D^{20} 1.5485; MR_D 79.091; computed. 78.766.

5.46 mg substance: 0.29 ml N_2 (24°, 753 mm). Found %: N 5.91.
$C_{17}H_{21}ON$. Computed %: N 5.49.

The hydrochloride of the dimethylaminoethyl ester of diphenylcarbinol (benadryl) was prepared by reacting an ether solution of the base with an ether solution of hydrogen chloride. Double recrystallization from an alcohol-ether mixture yielded colorless crystals with a m.p. of 163-164°.

4.45 mg substance: 0.19 ml N_2 (25°, 745 mm). Found %: N 4.67.
$C_{17}H_{21}ON \cdot HCl$. Computed %: N 4.80.

4. Diethylaminopropyl ester of diphenylcarbinol. This was synthesized by a similar procedure from 4.4 g of diphenylcarbinol, an alcoholic solution of sodium ethylate (0.6 g of sodium and 14 ml of absolute alcohol), and 4 g of diethylaminopropyl chloride. The excess diethylaminopropyl chloride was driven out of the reaction mixture in a 7-mm vacuum at 48-50°. The resulting ester was distilled at 180-182° and the same pressure as a slightly yellowish oil, which is readily soluble in ordinary organic solvents, but insoluble in water. The yield was 1.4 g (20% of the theoretical, though 36% if allowance is made for the diphenylcarbinol

recovered).

d_{20}^{20} 0.9205; n_D^{20} 1.487; MR_D 92.941; computed 92.573.

5.989 mg substance: 0.27 ml N_2 (19°, 724 mm). Found %: N 4.92.
$C_{20}H_{27}ON$. Computed %: N 4.71.

The hydrochloride of the diethylaminopropyl ester of diphenylcarbinol was prepared in the usual manner, being secured as highly hygroscopic, colorless crystals, which quickly deliquesce in air.

6.403 mg substance: 0.265 ml N_2 (24°, 747 mm). Found %: N 4.56.
$C_{20}H_{27}ON \cdot HCl$. Computed %: N 4.19.

5. Dimethylaminopropyl ester of diphenylcarbinol. This was prepared by the method outlined above – by reacting 3.2 g of diphenylcarbinol with an alcoholic solution of sodium ethylate (0.4 g of sodium and 10 ml of absolute alcohol) and 2.4 g of dimethylaminopropyl chloride. The excess dimethylaminopropyl chloride was driven off by distilling the reaction product in a 9-mm vacuum at 45-46°, the distillate at 180-182° being the dimethylaminopropyl ester of diphenylcarbinol, which is a light-yellow oil readily soluble in organic solvents and insoluble in water. The yield was 0.7 g (15% of the theoretical, or 32% in terms of the diphenylcarbinol entering into the reaction).

d_{20}^{20} 1.017; n_D^{20} 1.543; MR_D 83.40; computed 83.71.

4.266 mg substance: 0.21 ml N_2 (24°, 747 mm). Found %: N 5.20.
$C_{18}H_{23}ON$. Computed %: N 5.43.

The hydrochloride was secured as colorless, hygroscopic crystals, which deliquesced in air.

5.917 mg substance: 0.27 ml N_2 (19°, 724 mm). Found %: N 4.98.
$C_{18}H_{23}ON \cdot HCl$. Computed %: N 4.58.

6. Dimethyleminoethyl ester of benzyl alcohol. This was synthesized, like the esters of diphenylcarbinol, by reacting an alcoholic solution of sodium ethylate (0.5 g of sodium and 12 ml of absolute alcohol) with 2.3 g of benzyl alcohol and 2.5 g of dimethylaminoethyl chloride. The dimethylaminoethyl ester of benzyl alcohol is a colorless oil, freely soluble in organic solvents and insoluble in water, with a m.p. of 115-117° at 9 mm. The yield was 15% of the theoretical or 42% with allowance made for the benzyl alcohol recovered.

d_{20}^{20} 0.9687; n_D^{20} 1.5048; MR_D 54.986; Computed 54.782.

The hydrochloride of the ester, prepared in the usual manner by reacting an ether solution of the base with an ether solution of hydrogen chloride, consists of colorless crystals that had a m.p. of 82-184° after recrystallization from a mixture of alcohol and ether.

8.13 mg substance: 0.49 ml N_2 (24°, 747 mm). Found %: N 6.65.
$C_{11}H_{17}ON \cdot HCl$. Computed %: N 6.50.

7. Diethylaminopropyl ester of benzyl alcohol. This was prepared in the same manner from a solution of sodium ethylate (0.9 g of sodium and 22 ml of absolute alcohol), 4.4 g of benzyl alcohol, and 7 g of diethylaminopropyl chloride. A colorless oil, freely soluble in alcohol, ether, and benzene, but insoluble in water. B.p. 142-144° at 11 mm. The yield was 20%, or 40% of the theoretical in terms of the reacted benzyl alcohol.

d_{20}^{20} 0.9573; n_D^{20} 1.5068; MR_D 68.842; computed 68.670.

6.26 mg substance: 0.33 ml N_2 (24°, 747 mm). Found %: N 6.61.
$C_{14}H_{29}ON$. Computed %: N 6.89.

The hydrochloride of the diethylaminopropyl ester of benzyl alcohol consists of colorless, highly hygroscopic crystals that rapidly deliquesce in air.

5.626 mg substance: 0.29 ml N_2 (20°, 725 mm). Found %: N 5.63.
$C_{14}H_{29}ON \cdot HCl$. Computed %: N 5.31.

8. Dimethylaminopropyl ester of benzyl alcohol. This was prepared under the specified conditions from 4 g of benzyl alcohol, 5.2 g of dimethylaminopropyl chloride, and a solution of sodium ethylate (0.85 g of sodium and 20 ml of absolute alcohol), the yield being 20% of the theoretical, based upon the benzyl alcohol taken for the reaction and 36% based upon the quantity that was consumed. It is a colorless oil, freely soluble in organic solvents, though insoluble in water. M.p. 125-127° at 10 mm.

d_{20}^{20} 0.969; n_D^{20} 1.509; MR_D 59.606; computed 59.470.

2.141 mg substance. 0.15 ml N_2 (20°, 725 mm). Found %: N 7.65.
$C_{12}H_{19}ON$. Computed %: N 7.25.

The hydrochloride of the dimethylaminopropyl ester of benzyl alcohol was prepared as an oil, which crystallized when allowed to stand in a vacuum desiccator. The colorless crystals were highly hygroscopic, deliquescing in air, after being recrystallized from an alcohol-ether mixture.

4.197 mg substance: 0.23 ml N_2 (20°, 725 mm). Found %: N 6.24.
$C_{12}H_{19}ON \cdot HCl$. Computed %: N 6.10.

SUMMARY

This paper describes the synthesis of dialkyl amino ethyl and dialkyl amino propyl esters of phenyl- and diphenylcarbinol by reacting diphenylcarbinol and benzyl alcohol with the respective amino alkyl chlorides in the presence of an alcoholic solution of a sodium alcoholate.

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THE SPECTROPHOTOMETRY OF BIURET COORDINATION COMPOUNDS AS A METHOD OF PROTEIN RESEARCH

XII. SPECTROPHOTOMETRIC INVESTIGATION OF THE FORMATION OF A COPPER-BIURET COORDINATION COMPOUND IN THE PRESENCE OF A MIXTURE OF TWO PEPTIDES WITH DIFFERING CHAIN LENGTHS

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In our last report we showed how a mixture of three peptides (a glycyl di-, tri-, and tetrapeptide) behaved in the formation of a copper-biuret coordination compound. Our research results led to the conclusion that some peptides behave differently in a mixture than they do in individual solutions. In the present paper we had as our objective finding out which of these three peptides changes the nature of the coordination compound formed. It is most probable that it is the dipeptide that possesses this property. Apparently, this problem may be resolved by an investigation of the formation of a coordination compound in a mixture of two peptides, in which it is easier to follow the changes in the individual absorption curves. We have performed just such experiments.

1. Formation of Coordination Compounds in a 1:1 Mixture of a Tripeptide and a Dipeptide

A solution of a copper salt was gradually added to an alkaline solution of a tripeptide-dipeptide mixture (M:150 concentration). The change in the nature of the absorption was determined spectrophotometrically. The results are listed in Table 1 and plotted in Fig. 1.

The first to react is the tripeptide, coloring the solution purple. But the curve is not the same as the curve of an individual solution of the tripeptide coordination compound. The maximum is located at 550 mμ, instead of 575 mμ. This phenomenon cannot be attributed to the simultaneous partial formation of the dipeptide coordination compound, inasmuch as the latter has an absorption maximum at a wavelength of 670 mμ, and its being present would have shifted the maximum toward the longer wavelengths. It is much more likely that the coordination compound partially formed is of a mixed nature, its molecule containing both the tripeptide and the dipeptide. The formula of such a coordination compound might look like this.

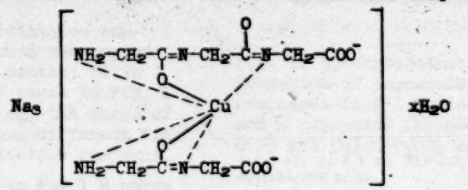

TABLE 1

Change in the Optical Density ε During the Gradual Formation of a Copper-Biuret Coordination Compound from a 1:1 Mixture of Glycyl Di- and Tripeptides (Concentration M:150)

Test No.	Wave length λ, mμ	Value of ε for 0.25 mol $Cu(CH_3COO)_2$			Arithmetical sum of ε for coordination compounds of the tri- and dipeptides
		I, 0.2 ml	II, 0.4 ml	III, 1.5 ml (excess)	
1	480	0.160	0.268	0.328	0.276
2	490	0.180	0.312	0.388	0.318
3	505	0.205	0.378	0.478	0.388
4	520	0.226	0.435	0.578	0.453
5	525	0.235	0.459	–	–
6	530	0.240	0.477	0.645	0.490
7	540	0.247	0.515	0.705	0.534
8	550	0.249	0.535	0.765	0.574
9	560	0.251	0.553	0.801	0.600
10	570	0.245	0.559	0.851	0.627
11	575	–	0.551	–	–
12	582	0.237	0.549	0.89	0.635
13	600	0.212	0.510	0.910	0.651
14	610	0.203	0.480	0.910	0.644
15	620	0.192	0.470	0.910	0.652
16	630	0.183	0.452	0.890	0.652
17	640	0.170	0.421	0.870	0.652
18	650	0.165	0.396	0.840	0.665
19	670	0.158	0.352	0.790	0.675
20	693	0.143	0.300	0.670	0.625
21	710	0.113	0.236	0.541	0.540
22	730	0.084	0.150	0.410	0.405

This coordination compound ought to have an absorption curve much like that of red coordination compounds, so that its presence would shift the maximum toward the shorter wavelengths. Adding more of the cooper salt to an alkaline solution of the tri- and dipeptides results in the formation of a coordination compound that is typical of a tripeptide (Curve II), even though the maximum for this coordination compound is located at 570 instead of 575 mμ.

The formation of coordination compounds comes to an end when the copper hydroxide is present in excess; it is represented by the upper curve in Fig. 1. The maximum lies at 610 mμ, the shape of the curve being altogether different from that of a protein coordination compound.

We have also plotted in Fig 1 a curve

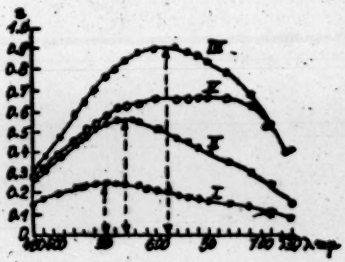

Fig. 1. Spectrophotometric curves of the formation of copper-biuret coordination compounds in a 1:1 mixture of a tri- and a dipeptide (M:150 concentration). 0.25 mol $Cu(CH_3COO)_2$ added. I-0.2 ml; II-0.4 ml; III-1.5 ml(excess); IV-arithmetical sum of ε.

representing the arithmetical sum of the optical densities ε for the individual solutions of copper-biuret coordination compounds of the tripeptide and the dipeptide, with a concentration of M:150. This curve does not coincide with the experimental aggregate curve, which lies much higher and has a maximum at a wavelength of 610 mμ, whereas the maximum is at 670 mμ for the arithmetical sum of ε.

Hence, we conclude that the tripeptide-dipeptide mixture gives rise to a mixture of coordination compounds that are not additive with respect to the absorption of light.

2. Formation of Coordination Compounds in a 1:1 Mixture of a Glycyl Tetrapeptide and Dipeptide

A solution of the copper salt was gradually added to a solution of a mixture of the tetrapeptide and the dipeptide (M:150 concentration). The change in the nature of absorption was determined spectrophotometrically. The results are given in Table 2 and Fig. 2.

TABLE 2

Change in the Optical Density ε During the Gradual Formation of a Copper-Biuret Coordination Compound in a 1:1 Mixture of a Glycyl Tetrapeptide and A Glycyl Dipeptide (Concentration M:150)

Test No.	Wave length λ, mμ	Values of ε — 0.25 mol $Cu(CH_3COO)_2$ added			Arithmetical sum of ε for coordination compounds of the tetra- and dipeptides
		I, 0.3 ml	II, 0.5 ml	III, 1.5 ml (excess)	
1	480	0.470	0.604	0.630	0.653
2	490	0.592	0.706	0.735	–
3	505	0.681	0.827	0.875	0.864
4	520	0.706	0.883	0.955	0.923
5	530	0.689	0.874	0.970	0.928
6	540	0.643	0.855	0.955	0.878
7	550	0.581	0.799	0.920	0.810
8	560	0.510	0.739	0.880	0.746
9	570	0.442	0.669	0.840	0.678
10	582	0.359	0.598	0.785	0.612
11	600	0.250	0.493	0.715	0.527
12	610	0.209	0.451	0.690	0.503
13	620	0.177	0.418	0.672	0.496
14	630	0.149	0.395	0.651	0.489
15	640	0.134	0.377	0.641	0.496
16	650	0.120	0.360	0.638	0.514
17	670	0.103	0.340	0.610	0.534
18	693	0.087	0.307	0.556	0.508
19	710	0.082	0.266	0.478	0.461
20	730	0.069	0.212	0.385	0.364

As we see from Fig. 2, Curve I, the tetrapeptide is the first to react, forming a typical red coordination compound. As more of the copper salt is added, more of the red coordination compound is formed, while part of the dipeptide begins to enter into the reaction, as indicated by Curve II, which exhibits a certain rise and point of inflection in the 610-730 mμ range. The final Curve III was plotted after copper hydroxide was present in excess, thus indicating that the formation of coordination compounds had come to an end. Curve III has one absorption maximum at the wavelength of 530 mμ and another incipient one between 650-670 mμ.

This curve has nothing in common with a curve for a protein coordination compound.

Curve IV is also plotted in Fig. 2, representing the arithmetical sum of the optical densities ε for the individual solutions of the copper-biuret coordination compounds of glycyl tetrapeptide and dipeptide, at a concentration of M:150.

Curve IV is not the same as Curve III; it is lower, and a second maximum is clearly evident at the wavelength of 660 mμ. The experimental mixture of coordination compounds (Curve III) exhibits a higher absorption, which indicates the absence of any additivity in the coordination compounds formed in the mixture of the tetrapeptide and the dipeptide. Here, as in the first case, it is obvious that the presence of the dipeptide changes the nature of the formation of coordination compounds.

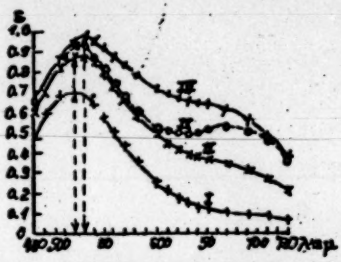

Fig. 2. Spectrophotometric curves of the formation of copper-biuret coordination compounds in a 1:1 mixture of tetra- and dipeptide (M:150 concentration). 0.25 mol $Cu(CH_3COO)_2$ added.
I-0.3 ml; II-0.5 ml; III-1.5 ml (excess); IV-arithmetical sum of ε.

3. Formation of Coordination Compounds in a 1:1 Mixture of a Glycyl Tetrapeptide and a Glycyl Tripeptide

The solution of the copper salt was gradually added to an alkaline solution of a mixture of the tetrapeptide and the tripeptide (M:150 concentration).

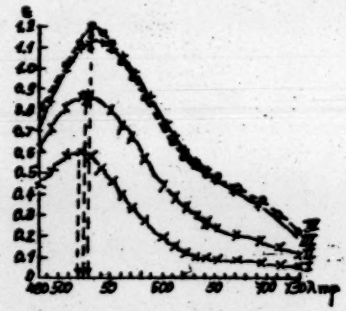

Fig. 3. Spectrophotometric curves of the formation of copper-biuret coordination compounds in a 1:1 mixture of a tetra- and tripeptide (M:150 concentration). 0.25 mol $Cu(CH_3COO)_2$ added.
I-0.3 ml; II-0.5 ml; III-1.5 ml (excess); IV-arithmetical sum of ε.

The change in the nature of the absorption of the resulting coordination compound is shown in Table 3 and Fig. 3. The first to react is the tetrapeptide, Curve I having a maximum at the wavelength of 520 mμ, corresponding fully to the curve for the individual coordination compound of the tetrapeptide. Then the tripeptide begins to react (Curve II), the maximum being shifted toward the longer wavelengths (530 mμ).

The end of the formation of coordination compounds, which is manifested by the appearance of an excess of copper hydroxide, is represented by Curve III. Curve III has an absorption maximum at 530 mμ, plus a certain rise and point of inflection in the 650-730 mμ region. It differs from the curve for a protein coordination compound.

Fig. 3 also reproduces Curve IV, which represents the arithmetical sum of the optical densities ε of the individual solutions of the biuret coordination compounds

TABLE 3

Change in the Optical Density ε During the Gradual Formation of a Copper-Biuret Coordination Compound in a 1:1 Mixture of a Glycyl Tetrapeptide and a Glycyl Tripeptide (M:150 concentration)

Test No.	Wave length, λ, mμ	Values of ε 0.25 mol $Cu(CH_3COO)_2$ added			Arithmetical sum of ε for coordination compounds of the tetra- and tripeptides
		I, 0.3 ml	II, 0.5 ml	III 1.5 ml (excess)	
1	480	0.446	0.604	0.710	0.821
2	490	0.515	0.704	0.840	-
3	505	0.591	0.820	0.990	1.096
4	520	0.609	0.872	1.10	1.19
5	525	0.597	0.880	1.12	-
6	530	0.589	0.888	0.135	1.212
7	540	0.524	0.848	0.130	1.176
8	550	0.473	0.816	1.10	1.12
9	560	0.406	0.736	1.06	1.048
10	570	0.347	0.680	0.99	0.971
11	582	0.277	0.568	0.90	0.863
12	600	0.190	0.441	0.748	0.722
13	610	0.164	0.383	0.670	0.645
14	620	0.134	0.335	0.605	0.592
15	630	0.115	0.295	0.553	0.539
16	640	0.102	0.272	0.505	0.514
17	650	0.093	0.248	0.468	0.475
18	670	0.084	0.215	0.415	0.419
19	693	0.078	0.183	0.354	0.363
20	710	0.065	0.147	0.278	0.303
21	730	0.056	0.104	0.185	0.227

of the tetrapeptide and the tripeptide. In contrast to the first two experiments, here we find that the curve representing the absorption of a mixture of coordination compounds of the tri- and the tetrapeptide (Curve III) is very close to the curve of the arithmetical sum of ε (Curve IV). This fact is highly significant. It indicates that the tripeptide and the tetrapeptide in a mixed solution behave altogether independently as far as the formation of coordination compounds is concerned.

EXPERIMENTAL

1. Experiment on the Formation of Coordination Compounds in a 1:1 Mixture of a Dipeptide and a Tripeptide

A solution was prepared as follows: 2 ml of a 0.05 molar solution of glycyl dipeptide + 2 ml of a 0.05 molar solution of glycyl tripeptide + 3 ml of 2N NaOH + 6.5 ml of H_2O. To this there was added a 0.25 molar solution of $Cu(CH_3COO)_2$, K = 0.9784, so that the solution contained 0.2 ml after Addition I, 0.4 ml after Addition II, and 1.5 ml after Addition III. This caused copper hydroxide to settle out, it being filtered out one hour later. Spectrophotometric measurements were made with a Kollemann spectrophotometer, Model 2. The results of the measurements are given in Table 1 and Fig. 1. The arithmetical sum of ε was secured as in our preceding report.

2. Experiment on the Formation of Coordination Compounds in a 1:1 Mixture of a Glycyl Tetrapeptide and Dipeptide

A solution was prepared as follows: 2 ml of a 0.05 molar solution of glycyl tetrapeptide + 2 ml of a 0.05 molar solution of glycyl dipeptide + 3 ml of 2N NaOH + 6.5 ml of H_2O. To this there was added a 0.25 molar solution of $Cu(CH_3COO)_2$ so that the solution contained 0.3 ml of the copper salt solution after Addition I, 0.5 ml after Addition II, and 1.5 ml after Addition III, which caused the precipitation of the excess copper hydroxide, which was filtered out after one hour had elapsed.

The spectrophotometric results are given in Table 2 and Fig. 2.

3. Experiment on the Formation of Coordination Compounds in a 1:1 Mixture of a Tetrapeptide and Tripeptide

A solution was prepared as follows: 2 ml of a 0.05 molar solution of glycyl tetrapeptide + 2 ml of a 0.05 molar solution of glycyl tripeptide + 3 ml of 2N NaOH + 6.5 ml of H_2O. The 0.25 molar solution of $Cu(CH_3COO)_2$ was added as in Experiment 2. The spectrophotometric results are given in Table 3 and Fig. 3.

SUMMARY

1. When a tripeptide and a dipeptide are present in a solution simultaneously, the biuret reaction results in the formation of a mixture of coordination compounds that is not a simple mixture of the coordination compounds of the individual peptides.

2. If the solution contains a tetrapeptide and a tripeptide at the same time, the biuret reaction will likewise result in the formation of a mixture of coordination compounds, the absorption curves of which indicate that they are not a mixture of the coordination compounds of the individual peptides.

3. Only when a tripeptide and a tetrapeptide are simultaneously present in a solution does the biuret reaction result in the formation of a mixture of coordination compounds that is a mixture of the coordination compounds of the individual peptides. The curve representing the absorption of light in such a solution may be plotted by arithmetically adding the optical densities of the individual solutions of the coordination compounds of the tetra- and the tripeptides in corresponding concentrations.

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THE SPECTROPHOTOMETRY OF BIURET COORDINATION COMPOUNDS AS A METHOD OF PROTEIN RESEARCH

XIII. ANALYSIS OF THE SPECTROPHOTOMETRIC CURVES OF BIURET-COPPER COORDINATION COMPOUNDS OF SERUM ALBUMIN, CASEIN AND GELATIN

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Our previous investigations of the formation of copper-biuret coordination compounds in various mixed peptide solutions have shown that only a mixture of a tetrapeptide and a tripeptide results in the formation of a simple mixture of coordination compounds of these peptides (in the other cases the reaction is complicated by the formation of some new coordination compounds). This phenomenon is so interesting and so important for our basic objectives – the study of the structure of the protein molecule – that we resolved to test it on a series of mixed solutions of a tetrapeptide and a tripeptide.

We prepared solutions that contained the following proportions of a tetra- and a tripeptide:

I	90% tetrapeptide	+ 10% tripeptide
II	70% tetrapeptide	+ 30% tripeptide
III	50% tetrapeptide	+ 50% tripeptide
IV	30% tetrapeptide	+ 70% tripeptide
V	20% tetrapeptide	+ 80% tripeptide
VI	10% tetrapeptide	+ 90% tripeptide.

For all these solutions we prepared solutions of biuret coordination compounds in the usual manner, which we then measured spectrophotometrically. Our results are given in Table 1 and in Figs. 1, 2, 3, 4, and 5. Moreover, we have plotted in each of these figures a curve representing the arithmetical sum of the ε of the solutions of the individual coordination compounds in corresponding concentrations and percentages. In every case the experimental curve coincides with the arithmetical sum of ε . Hence, any mixture of a tri- and a tetrapeptide actually gives rise to a simple mixture of the coordination compounds of these peptides, no matter what proportions are used. It is interesting to see how the location of the maximum and the entire shape of the curve change as the percentage of the tetrapeptide or of the tripeptide predominates in the solution.

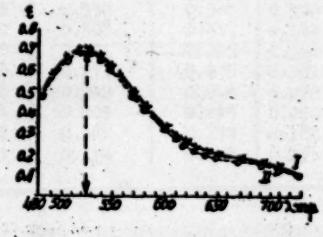

Fig. 1. 70% tetra- and 30% tripeptide.

I-Experiment; II-arithmetical sum of ε.

The curves for all the tri- and tetrapeptide mixtures that are reproduced separately in Figs. 1, 2, 3, 4, and 5, are plotted together in Fig. 6. The first thing we notice is the predominant influence of the red coordination compound of

TABLE 1

Optical Densities ε of Copper-Biuret Coordination Compounds of Various Mixtures of Glycyl Tri- and Tetrapeptides

Test No.	Wavelength λ, mμ	Value of ε					
		I	II	III	IV	V	VI
1	480	0.567	0.497	0.431	0.345	0.315	0.277
2	490	0.650	0.580	0.493	0.410	0.350	0.320
3	505	0.759	0.668	0.575	0.473	0.417	0.380
4	520	0.790	0.705	0.623	0.532	0.463	0.432
5	525	0.793	0.708	–	–	–	–
6	530	0.775	0.697	0.628	0.538	0.483	0.457
7	535	–	–	0.624	–	–	–
8	540	0.730	0.672	0.620	0.542	0.495	0.482
9	545	–	–	–	0.548	0.499	–
10	550	0.664	0.623	0.583	0.541	0.493	0.493
11	555	–	–	–	–	–	0.493
12	560	0.592	0.565	0.550	0.516	9.490	0.490
13	565	–	–	–	–	–	–
14	570	0.521	0.505	0.505	0.490	0.480	0.489
15	575	–	–	–	–	–	–
16	582	0.424	0.437	0.448	0,462	0.452	0.469
17	600	0.312	0.337	0.362	0.401	0.398	0.422
18	610	0.268	0.294	0.325	0.368	0.368	0.400
19	620	0.232	0.259	0.292	0.332	0.342	0.370
20	630	0.209	0.235	0.260	0.308	0.317	0.344
21	640	0.185	0.219	0.250	0.291	0.295	0.320
22	650	0.172	0.202	0.228	0.271	0.278	0.301
23	670	0.154	0.183	0.208	0.242	0.248	0.272
24	693	0.140	0.160	0.184	0.205	0.215	0.230
25	710	0.120	0.143	0.157	0.168	0.177	0.182
26	730	0.103	0.113	0.123	0.134	0.128	0.135

Fig. 2. 50% tetra- and 50% tripeptide.

x - experiment; o - arithmetical sum of ε.

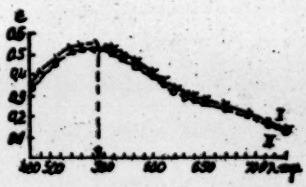

Fig. 3. 30% tetra- and 70% tripeptide.

I-experiment; II-arithmetical sum of ε.

the tetrapeptide upon the shape of the curve and the location of the maximum. Even for a mixture of 50% of the tetrapeptide and 50% of the tripeptide we get a mixture of coordination compounds in which the curve as a whole resembles those of red coordination compounds and possesses an absorption maximum at the wavelength of 530 mμ. The resemblence between the shape of Curve VI (for a mixture of 90% of the tripeptide and 10% of the tetrapeptide) to that of a protein coordination compound is striking.

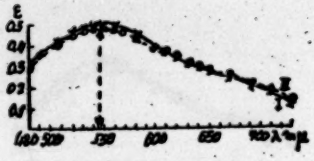

Fig. 4. 20% tetra- and 80% tripeptide.

I-Experiment; II-arithmetical sum of ε.

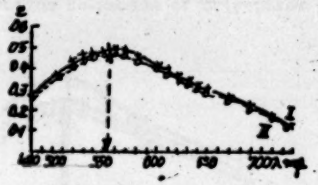

Fig. 5. 10% tetra- and 90% tripeptide.

I-Experiment; II-arithmetical sum of ε.

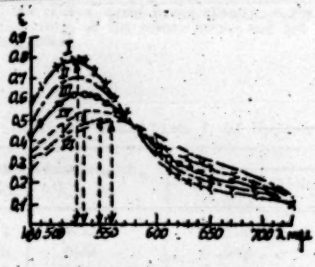

Fig. 6. Spectrophotometric curves of biuret copper coordination compounds of glycyl tetra- and tripeptides.

I-90% tetra- and 10% tripeptide; II-70% tetra- and 30% tripeptide; III-50% tetra- and 50% tripeptide; IV-30% tetra- and 70% tripeptide; V-20% tetra- and 80% tripeptide; VI-10% tetra- and 90% tripeptide.

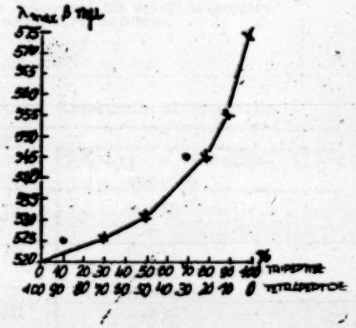

Fig. 7. $\lambda_{max.}$ as a function of the percentages of the tetra- and tripeptides.

If we lay off the percentage relationship between the tripeptide and the tetrapeptide along the axis of abscissas and the wavelength of the maximum absorption of the corresponding mixture along the axis of ordinates, we get a curve of the relationship between these variables such as the one reproduced in Fig. 7. The accuracy of this curve will, of course, depend largely upon the precision of the spectrophotometer. Use of this curve enables us to analyze an unknown solution, provided it contains a mixture of a tetrapeptide and a tripeptide in unknown proportions. As we see it, this is precisely the job of an analysis of the spectrophotometric curves of biuret coordination compounds of proteins. We used this method of investigation on several proteins. We did this by plotting spectrophotometric curves of the biuret coordination compounds of serum albumin, gelatin, and casein. Table 2 gives the values of the optical density ε for these coordination compounds. The absorption maximum for the coordination compound of serum albumin is located at the wavelength of 555 mμ. According to the curve in Fig. 7, a maximum at 555 mμ represents a 90%tripeptide + 10% tetrapeptide mixture of coordination compounds. We have plotted two curves in Fig. 8: I represents the curve for serum albumin, while II is the curve for a mixture of the coordination compounds of 90% tripeptide + 10% tetrapeptide. Curve I and II in Fig. 8 are very similar. The coordination compound of casein exhibits an absorption

Spectrophotometric Curves of Biuret-Copper Coordination Compounds of Tripeptide Mixtures

Fig. 8.

I-Dry powder, human serum albumin, 0.26% solution; II-mixture of 10% glycyl tetra- and 90% gycyl tripeptide.

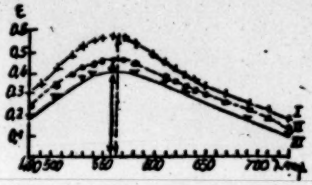

Fig. 9.

I-Gelatin, 0.26% solution; II-mixture of 7% glycyl tetra- and 93% glycyl tripeptide; III-casein, 0.24% solution.

TABLE 2

Optical Densities ε of Copper-Biuret Coordination Compounds of Proteins

Test No.	Wavelength, λ, mμ	Optical density ε			
		Serum albumin, 0.26%	Gelatin, 0.26%	Casein, 0.24%	93% tri- + 7% tetra-peptide
1	480	0.312	0.305	0.177	0.248
2	490	0.349	0.353	–	–
3	505	0.422	0.429	0.279	0.341
4	520	0.478	0.492	–	0.391
5	530	0.512	0.532	0.372	0.421
6	540	0.519	0.556	0.398	0.439
7	550	0.529	0.570	–	0.458
8	555	0.529	–	–	–
9	560	0.520	0.573	0.410	0.461
10	565	–	0.580	–	–
11	570	0.498	0.570	–	0.463
12	582	0.460	0.545	0.394	0.441
13	600	0.401	0.492	–	0.431
14	610	0.372	0.459	0.346	0.382
15	620	0.338	0.423	–	0.362
16	630	0.311	0.398	0.309	0.339
17	640	0.290	0.370	–	0.318
18	650	0.275	0.340	–	0.302
19	670	0.243	0.308	–	0.269
20	693	0.214	0.265	0.170	0.231
21	710	0.185	0.224	–	0.185
22	730	0.156	0.180	0.099	0.130

maximum at 560 mμ. The curve in Fig. 7 indicates that this position of the maximum represents a mixture of the coordination compounds of 93% of the tripeptide and 7% of the tetrapeptide. In Fig. 9 we have plotted the curves for the casein coordination compound for the mixture of coordination compounds of 93% tri- and 7% tetrapeptides. As we see in Fig. 9, the two curves are completely parallel and entirely similar. Curve I in the same figure represents the gelatin coordination compound. The position of the maximum on this curve, at the wavelength of 565 mμ, indicates that the percentage of tetrapeptides in this protein is still lower, totaling about 5%.

These results of the analysis of protein coordination compounds are of interest

not so much for their absolute values; they could be made more accurate, no doubt, if the sensitivity and the accuracy of the instrument used were increased. What is important for us in these experiments is the fact that in every case investigated the proteins exhibit a low percentage of red coordination compounds. The tripeptide plays the decisive role in determining the nature of the absorption of a protein coordination compound. But the protein structure must contain a tripeptide so that a violet coordination compound can be formed, inasmuch as the coordination compounds formed in a long chain are of the red tetrapeptide type.

All our investigations of the biuret coordination compounds of peptides and protein convince us that proteins contain a tripeptide. It is probably for that very reason that we are able to observe so farreaching an analogy between the formation of coordination compounds of a protein and a simple glycyl tripeptide, notwithstanding the complex amino-acid composition of proteins and the complicated structure of the protein molecule.

EXPERIMENTAL

1. Experiment on the formation of coordination compounds in mixtures of varying proportions of a tetrapeptide and a tripeptide. We prepared solutions of the biuret coordination compounds as follows: Solutions of the peptides (cf Table 3) were added to 2 ml of 2N NaOH, 2 ml of H_2O, and 1 ml of 0.25M $Cu(CH_3COO)_2$, the excess hydroxide being filtered out after 1 hour had elapsed and the solution being spectrophotometrically analyzed in the Kollemann instrument. The results are shown in Table 1.

TABLE 3

Composition of Peptide Mixtures

No.	Composition (ml of centimolar solutions of the peptides)		Percentage ratio of tetrapeptide to tripeptide
	Tetrapeptide	Tripeptide	
I	9	1	90%:10%
II	7	3	70%:30%
III	5	5	50%:50%
IV	3	7	30%:70%
V	2	8	20%:80%
VI	1	9	10%:90%
VII	10	–	100%:0%
VIII	–	10	0%:100%

2. Biuret coordination compounds of proteins. a) Biuret coordination compound of serum albumin. 4 ml of a 1% solution of serum albumin (prepared from dry powdered human serum) was mixed with 2 ml of 2N NaOH, 1.5 ml of 0.25M $Cu(CH_3COO)_2$, and 7.5 ml H_2O. The excess hydroxide was filtered out after 1 hour had elapsed. The albumin concentration was 0.26%. The solution was analyzed spectrophotometrically. The results are given in Table 2.

b) Biuret coordination compounds of gelatin. 4 ml of a 1% solution of gelatin was mixed with 2 ml of 2N NaOH, 1.5 ml of 0.25 M $Cu(CH_3COO)_2$, and 7.5 ml of H_2O. The solution was filtered after 1 hour had elapsed and then analyzed spectrophotometrically. Gelatin concentration was 0.26%. Results appear in Table 2.

c) Biuret coordination compounds of casein. This solution was prepared in the same manner as those above. The concentration was 0.24%. The results are listed in Table 2.

SUMMARY

1. A mixed solution of a tetra- and a tripeptide yields a simple mixture of the copper-biuret coordination compounds of the tetra- and tripeptides, no matter what their proportions.

2. Copper biuret coordination compounds of proteins, such as serum albumin, gelatin, and casein, are mixtures of tripeptide and tetrapeptide coordination compounds, with 90-95% tripeptides and 10-5% tetrapeptides.

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β-[2-PROPOXY(BUTOXY)NAPHTHOYL-6]-PROPIONIC ACIDS AND THEIR TRANSFORMATIONS

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We made use of the condensation of 2-propoxy(butoxy)naphthalenes with succinic anhydride in the presence of $AlCl_3$ to synthesize β-[2-propoxy(butoxy)naphthoyl]-propionic acids. The results of the reaction were not the same as those we had observed when we synthesized β-[2-methoxy(ethoxy)naphthoyl-6(1)]-propionic acids in the same manner from the corresponding esters of β-naphthol [1]. When we carried out the reaction in nitrobenzene, all we secured was β-(2-propoxynaphthoyl-6)- or β-(2-butoxynaphthoyl-6)-propionic acids, respectively, instead of the two isomeric ketonic acids we had expected, while condensation in carbon disulfide entailed so much tarring that we were unable to recover individual substances. Apparently, β-(2-alkoxynaphthoyl-1)-propionic acids with the higher alkyl radicals in the ester group are unstable in a Friedel-Crafts reaction. We have demonstrated the structure of β-[2-propoxy(butoxy)naphthoyl-6]-propionic acids by preparing their simplest derivatives (oximes, esters) and by converting them into compounds of known structure. For example, dealkylating these keto acids yielded 2-hydroxy-6-naphthoylpropionic acid, whereas dealkylating 2-propoxy(butoxy)naphthylbutyric acids, secured from these same keto acids by means of a Clemmensen reduction, yielded the well-known 2-hydroxy-6-naphthylbutyric acid.

EXPERIMENTAL

β-(2-Propoxynaphthoyl-6)-propionic acid. 103 g of 2-propoxynaphthalene, 61.8 g of succinic anhydride, and 1100 ml of anhydrous nitrobenzene were placed in a three-necked flask fitted with a mechanical stirrer. The reaction mixture was cooled externally with ice and salt, after which 194 g of aluminum chloride was added, with constant stirring, during the course of a day and a half. After addition was complete, stirring was continued for another 5 hours; the reaction mixture was decomposed with hydrochloric acid and ice and then filtered through a Buchner funnel. The small amount of substance remaining on the filter yielded 0.8 g of a colorless crystalline substance with a m.p. of 169-170° after recrystallization from 70% acetic acid. The filtrate was treated in the usual manner: the aqueous layer was separated from the nitrobenzene layer and washed with ether. The ether extracts were combined with the nitrobenzene layer, and the ether nitrobenzene solution was repeatedly washed with a 4% caustic soda solution. The alkaline solution was filtered and acidulated. The resulting precipitate yielded 26.5 g of a substance with a m.p. of 162-167° after desiccation and trituration with alcohol. Recrystallization from alcohol yielded β-(2-propoxynaphthoyl-6)-propionic acid with a m.p. of 169-170.5°, which was freely soluble in ether, benzene, and acetone, and crystallized from alcohol and from acetic acid.

3.565 mg substance: 9.327 mg CO_2; 2.004 mg H_2O. Found %: C 71.37; H 6.29
$C_{17}H_{18}O_4$. Computed %: C 71.33; H 6.29.

When 0.4 g of the β-(2-propoxynaphthoyl-6)-propionic acid thus prepared was heated with 9 ml of glacial acetic acid and 13 ml of hydrobromic acid and the reaction product treated in the usual manner, we secured 0.2 g of β-(2-hydroxynaphthoyl-6)-propionic acid with a m.p. of 227-229°.

2.830 mg substance: 6.890 mg CO_2; 1.251 mg H_2O. Found %: C 68.90; H 4.94. $C_{14}H_{12}O_4$. Computed %: C 68.85; H 4.92.

A sample of this substance, mixed with β-(2-hydroxynaphthoyl-6)propionic acid prepared by a different method exhibited no depression of the melting point.

Ethyl ester of β-(2-propoxynaphthoyl-6)-propionic acid. 1.5 g of the 2-propoxynaphthyl-6-propionic acid, 8 ml of absolute alcohol, and 0.7 ml of sulfuric acid were heated over a water bath for 6 hours. The usual treatment and recrystallization from alcohol yielded 1.1 g of the ethyl ester of the 2-propoxynaphthoyl-6-propionic acid as colorless crystals with a m.p. of 92-93.5°, which were freely soluble in organic solvents.

3.892 mg substance: 10.320 mg CO_2; 2.431 mg H_2O. Found %: C 72.31; H 6.98. $C_{18}H_{22}O_4$. Computed %: C 72.61; H 7.00.

Saponifying 1 g of the ethyl ester of 2-propoxynaphthoyl-6-propionic acid with an alcoholic solution of potassium hydroxide yielded 0.8 g of 2-propoxynaphthoyl-6-propionic acid with a m.p. of 169-170.5°.

Oxime of β-(2-propoxynaphthoyl-6)-propionic acid. 0.7 g of 2-propoxynaphthoyl-6-propionic acid, 0.54 g of hydroxylamine hydrochloride, 0.77 g of barium carbonate, and 20 ml of alcohol were heated for 6 hours over a water bath. After receiving the usual treatment, the resultant oily substance was triturated with a mixture of sulfuric and petroleum ethers and recrystallized from benzene; m.p. 140-142°.

5.290 mg substance: 0.213 ml N_2 (20°, 743.5 mm). Found %: N 4.59. $C_{17}H_{19}O_4N$. Computed %: N 4.62.

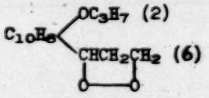
γ-(2-Propoxynaphthyl-6)-butyric acid. 1.8 g of 2-propoxynaphthoyl-6-propionic acid, 12 ml of toluene, 12 ml of glacial acetic acid, 12 ml of 1:1 hydrochloric acid, and 9 g of amalgamated zinc were placed in a round-bottomed flask fitted with a reflux condenser and boiled on a screen for 20 hours, a small quantity of 1:1 hydrochloric acid being added from time to time during the reaction. After heating was over, the cooled reaction mixture was shaken up with ether, and the ether solution was washed with a 10% solution of caustic soda. The alkaline solution was filtered and acidified with 10% hydrochloric acid. The resultant precipitate was crystallized from aqueous alcohol, yielding 0.7 g of 2-propoxynaphthyl-6-butyric acid as a colorless crystalline substance with a m.p. of 119.5-120.5°, which was freely soluble in ether, alcohol, and acetone.

4.024 mg substance: 11.100 mg CO_2; 2.754 mg H_2O. Found %: C 75.23; H 7.66. $C_{17}H_{20}O_3$. Computed %: C 75.00; H 7.36.

Ethyl ester of γ-(2-propoxynaphthyl-6)-butyric acid. 0.4 g of 2-propoxynaphthyl-6-butyric acid, 5 ml of absolute alcohol, and 0.2 ml of sulfuric acid were heated together for 6 hours. The usual treatment and recrystallization from alcohol yielded colorless crystals with a m.p. of 55-56°, which were freely soluble in organic solvents.

3.212 mg substance: 8.952 mg CO_2; 2.289 mg H_2O. Found %: C 76.01; H 7.97. $C_{18}H_{24}O_3$. Computed %: C 76.00; H 8.00.

γ-(2-Propoxynaphthyl-6)butyrolactone. 0.9 g of 2-propoxynaphthoyl-6-propionic acid, 20 ml of a 5% soda solution, and 10 ml of alcohol,* were placed in a glass jar fitted with a mechanical stirrer. 11 g of 20% sodium amalgam was gradually added, with constant stirring, a small quantity of 10% hydrochloric acid being added at intervals. Stirring was continued for 2 hours after all the sodium



*We later found that 2-propoxynaphthoyl-6 propionic acid could be reduced by sodium amalgam without adding alcohol.

amalgam had been added, after which the mercury was removed, the alcohol was driven off in vacuum, and a vaseline-like oil was extracted with ether. After the traces of ether had been eliminated from the alkaline solution, the latter was acidified with 10% hydrochloric acid until its reaction was strongly acid with Congo red, and then it was boiled for 10 minutes over a screen. The cooled reaction mixture was agitated with ether; the ether solution was washed with water and with a 3% solution of sodium bicarbonate and then desiccated with sodium sulfate. After the ether had been driven off, the residue was crystallized from alcohol. This yielded 0.35 g of a substance with a m.p. of 127.5-129°, which was freely soluble when heated in alcohol.

3.220 mg substance: 8.920 mg CO_2; 1.930 mg H_2O. Found %: C 75.55; H 6.70. $C_{17}H_{18}O_3$. Computed %: C 75.55; H 6.66.

β-(2-Butoxynaphthoyl-6)-propionic acid. The original substance – 2-butoxynaphthalene – was prepared by heating 150 g of β-naphthol, 450 g of butyl alcohol, and 60 g of sulfuric acid for 6 hours. This yielded 88 g of 2-butoxynaphthalene, with a m.p. of 31-33°. 88 g of aluminum chloride and 500 ml of anhydrous nitrobenzene were placed in a three-necked flask fitted with a mechanical stirrer. 50 g of 2-butoxynaphthalene and 28 g of succinic anhydride were added alternately, a little at a time, with constant stirring, to the resulting solution, which was chilled externally with a ice-salt mixture. When the addition was over, stirring was continued for 100 hours, after which the reaction mixture was decomposed by carefully pouring it out over ice and hydrochloric acid. The aqueous and nitrobenzene layers were separated, and the aqueous layer was agitated with ether, the ether solution being added to the nitrobenzene layer. The ether-nitrobenzene solution was washed with a 4% caustic potash solution, and the resulting alkaline solution was acidulated with 10% hydrochloric acid (after it had been washed with ether and filtered, and the traces of ether had been removed) until it was strongly acid with Congo red. This caused the precipitation of a tarry deposit, which was suction-filtered on a Buchner funnel and then dissolved in ether. The ether solution was washed with water and desiccated with sodium sulfate. Driving off the ether left behind a thick brown oil, which yielded 8.4 g of a substance with a m.p. of 145-148° after being triturated with alcohol. Crystallization from alcohol yielded 2-butoxynaphthoyl-6-propionic acid as colorless crystals with a m.p. of 150-152°, which were freely soluble in alcohol and acetone.

3.410 mg substance: 8.958 mg CO_2; 2.080 mg H_2O. Found %: C 71.64; H 6.83. $C_{18}H_{20}O_4$. Computed %: C 72.00; H 6.66.

Boiling 2-butoxynaphthoyl-6-propionic acid with a mixture of hydrobromic and acetic acids yielded 2-hydroxy-6-naphthoylpropionic acid, with a m.p. of 228-230°.

Ethyl ester of β-(2-butoxynaphthoyl-6)-propionic acid. 0.8 g of 2-butoxynaphthoyl-6-propionic acid, 10 ml of absolute ethyl alcohol, and 0.2 ml of sulfuric acid were heated together over a water bath. The usual treatment, followed by recrystallization from methanol, yielded the ethyl ester of the keto acid: a colorless crystalline substance with a m.p. of 82-83°, which is freely soluble in ether, ethyl alcohol, and acetone.

5.318 mg substance: 14.189 mg CO_2; 3.552 mg H_2O. Found %: C 72.77; H 7.47. $C_{20}H_{24}O_4$. Computed %: C 73.17; H 7.32.

Saponifying the ethyl ester of the keto acid with an alcoholic solution of caustic potash yielded 2-butoxynaphthoyl-6-propionic acid with a m.p. of 150-151.5°.

Butyl ester of β-(2-butoxynaphthoyl-6)-propionic acid. a) 0.5 g of 2-butoxynaphthoyl-6-propionic acid, 3 ml of butyl alcohol, and 0.2 ml of sulfuric acid

were boiled together over a screen for 6 hours. The usual treatment, followed by recrystallization from methanol, yielded the butyl ester of the keto acid: faintly colored crystals with a m.p. of 76-77.5°, freely soluble in ether, ethyl alcohol, and acetone.

2.780 mg substance: 7.573 mg CO_2; 1.983 mg H_2O. Found %: C 74.29; H 7.98. $C_{22}H_{28}O_4$. Computed %: C 74.16; H 7.86.

b) 8 ml of an alcoholic solution of caustic potash, 0.8 g of 2-hydroxynaphthoyl-6-propionic acid, and 6.5 g of butyl bromide were heated together over a water bath for 6 hours, after which the resultant potassium bromide and the potassium salt of the original acid were filtered out. The alcohol was driven out of the alcoholic filtrate in vacuum, and the residue was dissolved in ether. The ether solution was washed with water and desiccated with sodium sulfate. Driving off the ether and crystallizing the residue from methanol yielded a substance with a m.p. of 75-77°, which was freely soluble in ether, ethyl alcohol, and acetone.

Oxime of β-(2-butoxynaphthoyl-6)-propionic acid. We used 0.7 g of 2-butoxynaphthoyl-6-propionic acid, 0.54 g of hydroxylamine hydrochloride, 0.77 g of barium carbonate, and 20 ml of alcohol for this reaction. After having been recrystallized from alcohol, the oxime of 2-butoxynaphthoyl-6-propionic acid was a colorless crystalline substance that fused with decomposition at 143-145°.

4.400 mg substance: 10.985 mg CO_2: 2.659 mg H_2O. Found %: C 68.09; H 6.76. $C_{18}H_{21}O_3N$. Computed %: C 68.57; H 6.66.

γ-(2-Butoxynaphthyl-6)-butyric acid. 1.5 g of 2-butoxynaphthoyl-6-propionic acid, 10 ml of glacial acetic acid, 10 ml of toluene, 10 ml of hydrochloric acid (1:1), and 8 g of amalgamated zinc were boiled together for 20 hours, 1 ml of 1:1 hydrochloric acid being added three times. After the mixture had cooled, it was treated with ether. The ether solution was washed with a 4% solution of caustic soda, and the resulting alkaline solution was filtered and acidulated with 10% hydrochloric acid. The oily precipitate thrown down was crystallized from alcohol; this yielded 2-butoxynaphthyl-6-butyric acid as colorless crystals with a m.p. of 114-116°, freely soluble in ether and acetone.

3.000 mg substance: 8.288 mg CO_2; 2.104 mg H_2O. Found %: C 75.35; H 7.84. $C_{18}H_{22}O_3$. Computed %: C 75.52; H 7.69.

When 2-butoxynaphthyl-6-butyric acid is boiled with a mixture of hydrobromic and acetic acids, the alkoxy group is cleaved, as in the lower isomers, yielding 2-hydroxynaphthyl-6-butyric acid.

Ethyl ester of 2-butoxynaphthyl-6-butyric acid. 0.2 g of 2-butoxynaphthyl-6-butyric acid, 2 ml of absolute ethyl alcohol, and 0.1 ml of sulfuric acid (sp. gr. 1.84) were boiled together over a water bath for 6 hours. The usual treatment, followed by recrystallization from alcohol, yielded the ethyl ester of 2-butoxynaphthyl-6-butyric acid as a colorless crystalline substance with a m.p. of 49-50°, freely soluble in ether and acetone.

2.935 mg substance: 8.233 mg CO_2; 2.208 mg H_2O. Found %: C 76.50; H 8.42. $C_{20}H_{26}O_3$. Computed %: C 76.43; H 8.28.

When the ethyl ester of 2-butoxynaphthyl-6-butyric acid was boiled with a mixture of hydrobromic and acetic acids, the ester was saponified and the butoxy group cleaved, resulting in the formation of 2-hydroxynaphthyl-6-butyric acid.

γ-(2-Butoxynaphthyl-6)-butyrolactone. A solution of 1.5 g of 2-butoxynaphthoyl-6-propionic acid in a mixture of 30 ml of a 3% soda solution and 15 ml of alcohol was placed in a three-necked flask fitted with a mechanical stirrer. 17 g of 20% sodium amalgam was gradually added to the resultant solution, small quantities of hydrochloric acid being added from time to time during the reaction. The further treatment was the same as that described for the synthesis

of the lactone of 2-propoxy-6-hydroxybutyric acid. Recrystallization from alcohol yielded a colorless crystalline substance with a m.p. of 120-121°, freely soluble in organic solvents and insoluble in water.

4.568 mg substance: 12.744 mg CO_2; 2.843 mg H_2O. Found %: C 76.26; H 6.96. $C_{18}H_{20}O_3$. Computed %: C 76.05; H 7.04.

SUMMARY

1. β-[2-propoxy(butoxy)naphthoyl-6]propionic acids have been synthesized by reacting 2-propoxy(butoxy)naphthalenes with succinic anhydride in nitrobenzene in the presence of $AlCl_3$.

2. The structure of β-[2-propoxy(butoxy)naphthoyl-6]-propionic acids has been demonstrated by converting them into compounds whose structure is known.

3. γ-[2-Propoxy(butoxy)]butyrolactones have been synthesized.

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TRANSFORMATIONS OF LUCIGENIN

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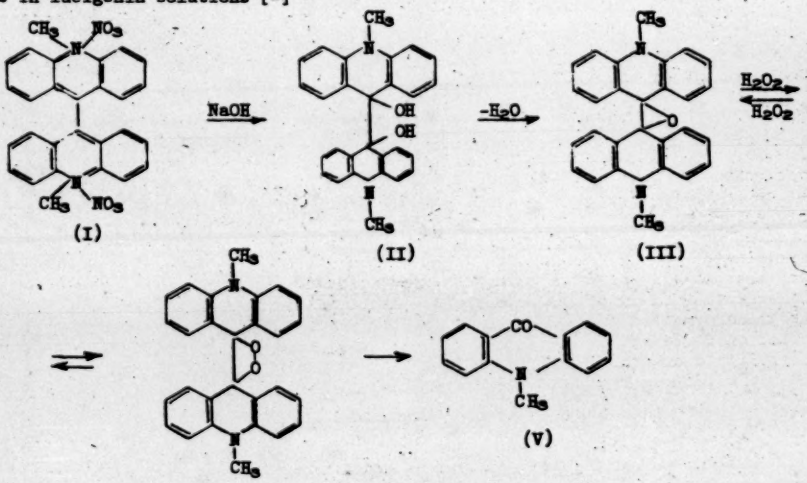
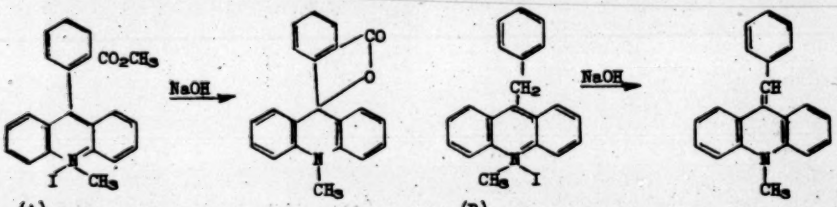
In 1934 it was discovered that when alkaline aqueous solutions of N,N'-dimethylbiacridilium nitrate are treated with hydrogen peroxide, visible light of extraordinary intensity and duration is emitted [1]. As a result of this discovery, N,N'-dimethylbiacridilium nitrate, which had been first synthesized in 1909 [2], was called lucigenin. This substance, together with luminol, is now a special object of study in the phenomenon of chemiluminescence in solutions. A number of papers have been published on problems involved in the physical and chemical transformations occurring in luminescent solutions of lucigenin [3-9]. Their results picture this process as extremely complicated, without any satisfactory explanation for it available as yet.

Gleu and Petsch represented the chemical conversions of lucigenin at the instant of luminescence by the following hypothetical diagram, allowing for various singularities and for the conditions under which chemiluminescence takes place in lucigenin solutions [1]



When an alkali acts upon N,N'-dimethylbiacridilium nitrate (I), the latter is converted into a carbinol base (a pseudobase) (II), from which more water is split off to form the oxide (III). Hydrogen peroxide converts the oxide into a peroxide (IV). The authors assume that this last transformation is reversible,

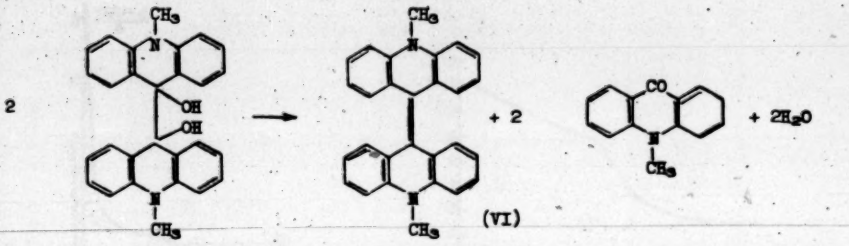
the luminescence phase corresponding to the phase in which the peroxide (IV) is reconverted to the oxide (III). At the same time (IV) may decompose, being converted into N-methylacridone (V), which is supposed to put an end to the chemiluminescence. Up to the present time not one of the stages of this diagram has received any experimental corroboration. The probability of the hypothetical transformations (I) → (II) → (III) cited in the above diagram is supported by such well-known examples of the conversions of quaternary salts of the acridines as the formation of a lactone from the methyl ester of acridine-9-phenyl-o-carboxylic acid methiodide (A) and of 9-benzylidine-N-methylacridan (B) from 9-benzylacridine methiodide by reacting solutions of (A) and (B) with an alkali [10].



Decker and Petsch [3] have tried to trace the chemical transformations of lucigenin in aqueous solution; they found that the reaction was a complicated one. The only product they managed to isolate was N-methylacridone, which they assumed was the end product of all the transformations involved. These authors found it more appropriate to assume the formation of an intermediate monopseudobase rather than a dicarbinol base as an explanation for the luminescent reaction, inasmuch as the latter base ought to be a stable compound according to these author's ideas regarding compounds of this nature, whereas the action of an alkali upon lucigenin in the luminescence test yields an easily changed base that is sensitive to reducing and oxidizing agents and is formed only after the reaction, together with the least stable products. Tamamushi and Akiyama [4] used benzene to extract a substance formed when an aqueous solution of lucigenin was reacted with an alkali. The authors described the strongly fluorescent substance in the benzene as highly unstable in the presence of atmospheric oxygen. They assumed that an intermediate biradical, N,N'-dimethylbiacridene, which is supposed to be readily oxidized even by atmospheric oxygen and the peroxide (IV), participates in the reaction involving the emission of light. Gleu and Nitzsche deny that this is possible with N,N'-dimethylbiacridene, as they found it to be diamagnetic [8]. Nitzsche's paper [11] mentions a more specific observation on the transformation of lucigenin, (with a reference to Schaarschmidt's 1938 dissertation). He states that in aqueous alkaline solutions the lucigenin pseudobase (II) is disproportionated into N,N'-dimethylbiacridene (VI) and N-methylacridone, which may be represented as follows: (See page 655.)

There is no description of any experimental data in the literature to support this reaction.

Gleu and his associates [8] synthesized a number of substituted biacridylium salts: 1,1', 2,2', 3,3', and 4,4'-methyl and methoxy derivatives and N,N'-diethyl and N,N'-diphenyl analogs of lucigenin. The chemiluminescence in the solutions of these new salts was no more intense than the chemiluminescence of lucigenin. Gleu and his associates synthesized most of these compounds by oxidizing the respective N,N'-dimethylbiacridenes with nitric acid. The authors found that the latter (water-insoluble) compounds likewise exhibit beautiful luminescence when



dissolvedin organic solvents. In the latter cases chemiluminescence occurs without the addition of any alkali or hydrogen peroxide, merely as the result of autooxidation. Particularly bright luminescence was found in solutions of 3,3'-dimethoxy-N,N'-dimethylbiacridene. The authors believe that the chemiluminescence of N,N'-dialkyl biacridenes and that of quaternary biacridylium salts are most likely related, but no explanation has been given of this as yet.

The foregoing survey exhausts the data in the literature on the observed and conjectural transformations of lucigenin in a chemiluminescent reaction. In our research we set as our objective the furnishing of experimental proof concerning which of the lucigenin transformation products is involved in the luminescence reaction. Our experiments gave a negative answer to the question of whether the diquaternary base of lucigenin participates itself in the luminescent reaction. We secured a solution of the diquaternary base (II) by reacting an aqueous solution of lucigenin bromide with silver oxide. No luminescence was produced when this solution was reacted with hydrogen peroxide. Chemiluminescence did occur, however, when hydrogen peroxide and a solution of a caustic alkali were added to a solution of the diquaternary base. This observation disproves Decker's and Petsch's supposition that a monopseudobase participates in the chemiluminescence reaction and, on the other hand, indicates that this reaction involves a substance formed from the diquaternary base by the action of an alkali.

When solutions of the diquaternary base of lucigenin are left to stand, they undergo a change, a precipitate settling out gradually. This change is in conformity with the drop in the conductance of solutions of this base and with potentiometric measurements. The results of these measurements are shown in Figs. 1 and 2. We recovered lucigenin bromide almost quantitatively from a freshly prepared solution of the diquaternary base by neutralizing it with hydrobromic acid. Correspondingly, we recovered half of the lucigenin salt used for the experiment in the same manner from a solution of the base that had stood for 5 hours and had lost half of its initial contents, to judge by the titration data. To judge by the drop in conductance, a solution of the lucigenin base that had been kept for 5 hours contained only a negligible quantity of the original true base. This indicates that such a solution contains a carbinol base.

As we see from the titration results reproduced in Fig. 2, a 0.02N solution of the lucigenin base still contains a small portion of the base to be titrated with hydrochloric acid after having been kept for 3 days. In a chemiluminescence test, such a solution produces luminescence of nearly normal intensity when reacted with an alkali and H_2O_2, as compared to the luminescence of a solution of lucigenin bromide of equivalent concentration. To judge by the titration results, the concentration of the base in the solution that had stood for 72 hours is still higher than the concentration of lucigenin that was found to be an optimum for the

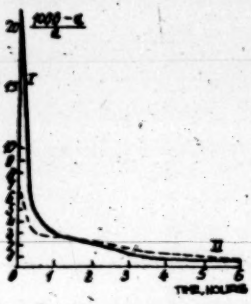


Fig. 1. Conductance of solutions of the lucigenin base: I - 0.02N; II - 0.005N.

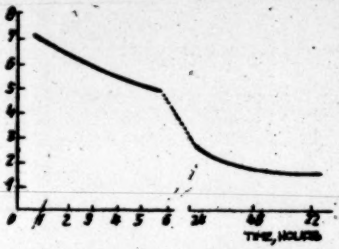
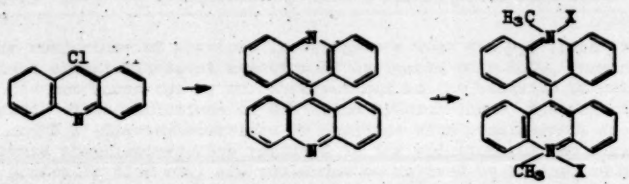


Fig. 2. Titration (potentiometric) of 50 ml of a 0.02N solution of the lucigenin base with a 0.1N HCl solution.

production of the highest luminescence intensity in terms of lucigenin concentration in Sveshnikov's experiments [9]. We were unable to isolate any individual substances when we analyzed the precipitate that settled out of the lucigenin base solution upon standing. Still we can state that the precipitate did not contain N-methylacridone. This conclusion is supported by the insolubility of the precipitate in alcohol and the absence in the alcoholic filtrate of the light-blue fluorescence that is characteristic of N-methylacridone and is manifested when even an infinitesimal amount of known N-methylacridone is added to the solution. We endeavored to isolate the diquaternary base of lucigenin from its aqueous solution. We were unsuccessful. Instead of the diquaternary base we always got a substance that was insoluble in water and could not be reconverted into lucigenin bromide by neutralizing it with hydrobromic acid. For example, when we poured a freshly prepared solution of the diquaternary base into alcohol, we got a copious precipitate of a substance that consisted of short yellow prisms after recrystallization from pyridine, which were insoluble in water and melted with decomposition at 260-262°. We isolated the same substance almost quantitatively by reacting an alcoholic solution of lucigenin bromide with a solution of a caustic alkali. The results of analysis of this substance are in good agreement with the data computed for the compound that may exist under these conditions: N,N'-dimethyl-9,9'-biacridene oxide (III). The oxide is only sparingly soluble in alcohol, though much more soluble in pyridine. A solution of the oxide in methanol emits a faint light when heated without hydrogen peroxide, while a solution of the oxide in pyridine emits a very bright yellow-green light after hydrogen peroxide has been added. This emission is identical with the chemiluminescence of lucigenin. When heated with dilute nitric acid, the oxide is reconverted into lucigenin (the nitrate). We found no changes occurring in the oxide (such as disproportionation, giving rise to N,N'-dimethylbiacridene and N-methylacridone, or the like), when its solutions in pyridine were heated for a long time (4 hours). The substance proved to be unstable when its sclutions in other solvents, such as chlorobenzene, were heated. As such a solution boiled, a dark-red, nonhomogeneous precipitate settled out. The structure of the compound was demonstrated by its behavior when heated with glacial acetic acid. The substance dissolved, though it was not thrown down when the solution was diluted with water. Evidently, heating with acetic acid ruptures the oxide ring of the substance, forming the water-soluble N,N'-dimethylbiacridylium diacetate. Lucigenin iodide, which is only sparingly soluble in water, is

thrown down from such a solution by adding a solution of potassium iodide to it. We secured the identical iodide by adding a solution of potassium iodide to a solution of lucigenin bromide in glacial acetic acid, heated to the boiling point.

The usual method of synthesizing lucigenin is to prepare it from N-methylacridone, via N,N'-dimethylbiacridene, as described by Decker and Dunant [2,7,12]. Gleu and his associates worked out a new variant of the synthesis of lucigenin and its analogs, starting with N-alkyl acridones and employing an organomagnesium synthesis [13]. We found it most convenient to prepare the quaternary biacridylium salts required in our investigations from the corresponding biacridines, the preparation of which we have recently described [14]. Our earlier observation concerning the formation of biacridines from mesochloroacridines by means of Raney's nickel may now be supplemented by our new observation: the same condensation may be effected with zinc (zinc dust), the other conditions remaining the same. With unsubstituted biacridine this new method yields results that are somewhat worse than those secured with the nickel. In the synthesis of a substituted biacridine, 3,3'-dichlorbiacridine, the zinc synthesis produces the same yield of high-quality product as the nickel. Lehmstedt and Hundertmark [15] found that, in contrast to acridine, biacridine is N-methylated by dimethyl sulfate with much more difficulty (the yield being only 50% after 10 hours of heating to 185°). Our observations contradict this assertion. When biacridine is heated to boiling with an excess of dimethyl sulfate, the reaction is complete after only 2 hours of heating. And as little as 15 minutes of heating in boiling dimethyl sulfate suffices for a substituted biacridine. The yield of the biacridylium salt, carefully purified after the reaction, was as much as 80% of the theoretical. The mesochloroacridines are available compounds, the synthesis of which has been thoroughly canvassed [16]. The feasibility of converting the mesochloroacridines into biacridines by means of zinc or Raney's nickel and of converting the latter into dimethylbiacridylium salts, now demonstrated, represents, by and large, a new and easily accessible variant of the synthesis of lucigenin and its analogs.



We prepared N,N'-dimethylbiacridene and N,N'-dimethylbiacridan in order to study their behavior in a chemiluminescent reaction, compared to that of the oxide described above. Decker and Dunant recommended that N,N'-dimethylbiacridene be synthesized by crystallizing the product of reducing N-methylacridone with zinc. Gleu and his coworkers used this method to synthesize dialkyl biacridenes. We have found a new way of synthesizing N,N'-dimethylbiacridenes, involving the treating of biacridylium bromides with Raney's nickel. This method is distinguished by its ease and the high yields of biacridenes. We demonstrated the general nature of the conversion of 9-chloroacridines into biacridines, of the latter into quaternary biacridylium salts, and of the latter, in turn, into dimethylbiacridene oxide and dimethylbiacridene by synthesizing analogous compounds, starting out with 6,9-dichloroacridine. The chemical properties of N,N'-dimethyl-3,3'-dichlorobiacridene oxide and N,N'-dimethyl-3,3'-dichlorobiacridene resemble those of the corresponding compounds with no chlorine substituents. The chemiluminescence of solutions of N,N'-dimethyl-3,3'-dichloro-9,9'-biacridene oxide differs from that of N,N'-dimethylbiacridene oxide. It appears under the same conditions as for the oxide that is not chlorine-substituted, but under these conditions it is not

as bright nor does it last as long. But under different conditions it surpasses in some respects the chemiluminescence of the compound that is not chlorine-substituted. The oxide of the chlorine analog dissolves readily in toluene. When this solution is diluted with methanol, an intense yellow-green luminescence appears (without H_2O_2:), which is steady and lasts very long (1.5 hours). In contrast, no chemiluminescence occurs in a solution of N,N'-dimethyl-3,3'-dichloro-9,9'-biacridene under the same conditions or even when a drop of H_2O_2 is added. Investigation of the physical mechanism involved in the luminescence of the oxide of the chlorine analog of lucigenin, which is displayed without the action of an alkali or of H_2O_2, is obviously of heightened interest. We shall describe the synthesis and the properties of the chlorine analogs of lucigenin in detail in our next report.

Semon and Graig [17] secured N,N'-dimethylbiacridan together with 9,10-dimethylacridan by reacting acridine methiodide with methylmagnesium iodide. We prepared N,N'-dimethylbdacridan with a high yield by dehalogenating acridine methylbromide with Raney's nickel. The formation of biacridines from mesochloroacridines, investigated and described by us in detail previously [14,18], were the first instances of this phenomenon.

Solutions of N,N'-dimethylbiacridan are not fluorescent.

When hydrogen peroxide is allowed to act upon a solution of N,N'-dimethylbiacridan in pyridine, no chemiluminescent reaction takes place. Apparently, a certain state of the 9,9' carbon bonds in the twinned N-methylacridyl radicals present in N,N'-dimethylbiacridene and N,N'-dimethylbiacridene oxide is required for the chemiluminescent reaction to start.

It should be noted that the 9,9' bond is more highly stable in these latter compounds. N,N'-dimethylbiacridan, for example, is readily oxidized by dilute nitric acid to N-methylacridone, whereas N,N'-dimethylbiacridene and its oxide are merely converted quantitatively into a biacridylium salt under the same conditions.

The conjecture of previous investigators that the 9,9'-bond is readily ruptured in a chemiluminescent reaction of lucigenin with H_2O_2, forming N-methylacridone, is not borne out by our observations on the behavior of related compounds. We treated boiling solutions of N,N'-dimethylbiacridene, N,N'-dimethylbiacridene oxide, and N,N'-dimethylbiacridan in pyridine with considerable excesses of H_2O_2. The intense chemiluminescence produced in the solutions of the first two compounds gradually died away and could not be revived by adding new batches of H_2O_2. No N-methylacridone was found in any of these instances, not even with N,N'-dimethylbiacridan (which is readily oxidized at the 9,9' bond by dilute nitric acid). Only in the case of N,N'-dimethylbiacridene oxide did a light-blue chemiluminescence occur when the reaction solution was diluted with water, though no N-methylacridone was found in the precipitate thrown down. In blank tests the N-methylacridone placed in the solution earlier was recovered from the solution almost quantitatively, even when the quantity employed was extremely minute. This casts doubt upon the latter stages of the transformations of lucigenin in the chemiluminescent reaction as conjectured in Gleu's diagram.

Dilution of the pyridine solutions of N,N'-dimethylbiacridene and N,N'-dimethylbiacridene oxide with water, after they had been treated with an excess of hydrogen peroxide and the resulting prolonged chemiluminescence had stopped, yielded the substances contained in these solutions. In each case they proved to be the same as the original substances: N,N'-dimethylbiacridene or N,N'-dimethylbiacridene oxide. This important observation indicates that in spite of the presence of an initial substance that can produce a chemiluminescent reaction in the solution, the reaction does not take place even when hydrogen peroxide is present. After the original substance had been recovered (N,N'-dimethylbiacridene

or N,N'-dimethylbiacridene oxide as the case may be), the chemiluminescence can be repeated in identical fashion by dissolving the substance in pyridine and adding hydrogen peroxide to the solution. It follows from this observation that the original pyridine solution of the substance – N,N'-dimethylbiacridene or N,N'-dimethylbiacridene oxide – contains some different molecules that act as catalysts in the mechanism of decomposing the hydrogen peroxide, causing the emission of light; as these molecules are used up the chemiluminescent reaction dies away. Study of this phenomenon by physical methods may confirm this supposition concerning the nature of this process, and this is also the road to a considerable increase in the intensity of the chemiluminescence of acridine derivatives.

EXPERIMENTAL

Synthesis of 3,3'-dichloro-9,9'-biacridine from 6,9-dichloroacridine with zinc. 7 g of 6,9-dichloroacridine (m.p. 168-169°) and 1.4 g of zinc dust were placed in 175 ml of methanol. The mixture was heated until the alcohol gently boiled for four hours, with constant stirring. The substance did not dissolve, the suspended substance turning yellow. Upon cooling, the solid substance was filtered out and washed on the filter with methanol. The dry precipitate weighed 5.7 g. The precipitate was boiled with pyridine (300 ml). The hot solution was filtered, the unreacted zinc dust (0.4 g) remaining on the filter. The pyridine solution was diluted with water until all the precipitate had been thrown down. The precipitate was filtered out, carefully washed on the filter with water, and dried. This yielded 5 g of dichlorobiacridine as a white amorphous powder with a cream-colored tinge (80% of the theoretical yield). No traces of 3-chloroacridone were found when a sample of this substance was boiled with an alcoholic alkali. The substance fused at 346-347° after having been washed with alcoholic alkali and water and then desiccated.

0.0795 g substance: 0.0537 g AgCl (Carius). Found %: Cl 16.71.
$C_{26}H_{14}N_2Cl_2$. Computed %: Cl 16.67.

Synthesis of 9,9'-biacridine from 9-chloroacridine. 5 g of 9-chloroacridine (m.p. 117-118°) and 5.0 g of zinc dust were placed in 125 ml of methanol. The mixture was heated with constant stirring, until the alcohol gently boiled for four hours. The substance entered solution at first, but as heating continued a green precipitate was thrown down. After cooling the precipitate was filtered out and washed on the filter with methanol. The dry precipitate weighed 7.2 g. It was boiled with 300 ml of pyridine, and the solution filtered while hot. The unreacted zinc dust (3 g) remained on the filter. The substance was recovered from the pyridine solution by diluting the latter with water. This yielded 3.4 g of washed, dried, crude biacridine; from this we secured 1.8 g of the pure biacridine by purification via the hydrochloride, which represented 43% of the theoretical yield (not allowing for the loss of the substance in the mother liquors during purification).

Lucigenin bromide (N,N'-dimethylbiacridylium bromide). A mixture of 7.7 g of biacridine and 27 ml of anhydrous neutral dimethyl sulfate was heated for 2 hours with a reflux condenser while the dimethyl sulfate gently boiled. After cooling the reaction mass was diluted with ether (60 ml), and the ether layer was decanted from the semi-solid precipitate that was thrown down; the latter was again washed with 60 ml of ether and then dissolved in 100 ml of water. The aqueous solution of the salt was heated to drive off the ether and break down the residual dimethyl sulfate, after which charcoal was added, and the solution was filtered. A hot solution of potassium bromide (70 g of KBr in 100 ml of water) was added to the warm solution of the methosulfate. The precipitated salt was filtered out of the still warm solution, washed on the filter with water (20 ml), and dried at 70°. This yielded 10.1 g of the salt, or 80% of the theoretical

yield. The bromide was again recrystallized from methanol (1:10) for analysis and for individual experiments; it is thrown down as golden leaflets that are readily soluble in hot water, soluble in alcohol, and insoluble in ether.

0.5740 g substance: 0.054 g lost in drying (100-110°); 0.1726 g substance: 5.6 ml 0.1N $AgNO_3$ (potentiometrically). Found %: H_2O 9.40; Br 25.9. $C_{28}H_{22}N_2Br_2 \cdot 3H_2O$. Computed %: H_2O 9.00; Br 26.62.

When the water of crystallization is removed, the salt turns red, turning yellow again in storage; it loses methyl bromide at 250-270°, being converted into a subliming biacridine (m.p. 392-393°). When the bromide is heated with 6% nitric acid (1:40), an orange-yellow solution is formed, from which the yellow leaflets of lucigenin nitrate settle out upon cooling. The lucigenin was recrystallized from water (1:5), dried in a desiccator to constant weight, and then analyzed.

4.173 mg substance: 0.408 mg N_2 (23.5°, 723 mm). 3.533 mg substance: 8.499 mg CO_2; 1.331 mg H_2O. Found %: C 65.61; H 4.22; N 10.69. $C_{28}H_{22}O_6N_4$. Computed %: C 65.87; H 4.34; N 10.97.

Lucigenin nitrate is much less soluble in boiling methanol than the bromide (1:50 and 1:10, respectively); in water, on the other hand, it is the nitrate that is more highly soluble (1:3 in boiling water as against 1:8 for the bromide).

N,N'-dimethyl-3,3'-dichlorobiacridylium bromide. A mixture of 5 g of 3,3'-dichloro-9,9'-biacridine and 18 ml of dimethyl sulfate was boiled until the components formed a solution. The solution was heated for 15 minutes, with the dimethyl sulfate boiling gently. After the reaction mixture had cooled, 40 ml of ether was added to it; the ether layer was decanted from the precipitate that formed, and the latter was washed again with 40 ml of ether. The semisolid methylation product was dissolved in 60 ml of water, the solution was gradually heated to a boil, charcoal was added, and the solution was filtered. A hot solution of potassium bromide (42 g of KBr in 60 ml of water) was added to the filtrate. The N,N'-dimethyl-3,3'-dichloro-9,9'-biacridylium bromide that settled out as a dark-yellow crystalline powder when the solution cooled was filtered out, again dissolved in 50 ml of water, and reprecipitated by adding a hot solution of potassium bromide (35 g of KBr in 30 ml of water). The reprecipitated salt was filtered out of the warm mother liquor again, washed on the filter with 15 ml of water, and dried at 60-70°. This yielded 5.3 g of the dry dimethyldichlorobiacridylium bromide as a yellow-orange, finely crystalline powder, or 70% of the theoretical yield. Some more of the substance can be secured by concentrating the aqueous mother liquors. Crystallization from methanol (1:10) yielded two-thirds of the bromide used as yellow-orange crystals.

0.3653 g substance: 0.0494 g loss in drying (100-110°). 0.1932 g substance: 5.8 ml 0.1N $AgNO_3$ (potentiometrically). 0.2116 g substance: 0.2003 g AgCl + AgBr (Carius). Found %: Br 23.99; H_2O 8.72. $C_{28}H_{20}N_2Cl_2Br_2 \cdot 3H_2O$. Computed %: Br 23.88; H_2O 8.08. Computed AgCl + AgBr 0.2090 g.

The properties of N,N'-dimethyl-3,3'-dichloro-9,9'-biacridylium bromide resemble those of lucigenin bromide; they differ in their behavior during a chemiluminescent reaction.

Preparation of 0.02N and 0.05N solutions of the diquaternary base of lucigenin. Silver oxide was prepared from an aqueous solution of 9 g of $AgNO_3$ and 60 ml of a 10% NaOH solution; the oxide was carefully and repeatedly washed with distilled water, after which a solution of 3 g of lucigenin bromide in 90 ml of water was added to it. The precipitated silver bromide was filtered out at once; the filtrate was a 0.1 N solution of the lucigenin base (110 ml).

Diluting it with water to make up 550 ml yielded a 0.02N solution of the lucigenin base. This solution was divided into 50-ml batches, the conductance of which was measured at definite intervals of time, while they were titrated potentiometrically with a 0.1N solution of hydrochloric acid. The original 0.1N solution of the base, both freshly prepared and after standing for 5 hours, was used to recover the lucigenin bromide from the solution by acidulating it with hydrobromic acid. The solution acidulated with HBr was evaporated to dryness, and the residue was recrystallized from water (1:8).

N,N'-Dimethyl-9,9'-biacridene oxide. 8 g of lucigenin bromide was dissolved in 280 ml of methanol. The orange-yellow solution of the salt was chilled, and 130 ml of a 40% caustic soda solution was gradually added. The precipitate that settled out of the darkened solution was filtered out and washed on the filter with methanol and with water until it no longer manifested any reaction with phenolphthalein. This yielded 5.3 g of a dry yellow-green precipitate; it was recrystallized from 70 ml of pyridine. The crystals that settled out as the pyridine solution cooled were filtered out, washed with alcohol and with ether, and desiccated over H_2SO_4 in an exsiccator. This yielded 4.3 g of N,N'-dimethyl-9,9'-biacridene oxide as bright-yellow crystals (short hexagonal prisms under the microscope), with a m.p. of 260-262°.

5.847 mg substance: 0.3724 ml N_2 (17.5°, 728 mm). 4.317 mg substance: 13.250 mg CO_2; 2.250 mg H_2O. Found %: C 83.70; H 5.63; N 7.17. $C_{28}H_{22}ON_2$. Computed %: C 83.55; H 5.51; N 6.96.

We also secured the same substance by reacting lucigenin nitrate with an alcoholic alkali under the same conditions. Dimethylbiacridene oxide is slightly soluble in alcohol, insoluble in water or ether, slightly soluble when heated in benzene (1:300), and much more soluble in dioxane (1:25). In contrast to N,N'-dimethylbiacridene, it undergoes no change when treated with bromine water, nor is it changed when heated with an alcoholic 5% solution of hydrochloric acid. Boiling it with 6% nitric acid converts it into lucigenin nitrate, as is the case with N,N'-dimethylbiacridene. The luminescence of a dilute pyridine solution of the oxide when treated with hydrogen peroxide is the same in nature, color, and duration as the luminescence of lucigenin when its aqueous solution of the same concentration is treated with alkali and hydrogen peroxide.

N,N'-Dimethyl-9,9'-biacridene. 2 g of lucigenin bromide was dissolved in 50 ml of methanol; 4 g of Raney's nickel was added to the solution. The mixture was heated to boiling for 3 hours with constant stirring. After the reaction mass had cooled, the precipitate was filtered out and treated with 300 ml of boiling pyridine. After the filtrate had cooled, a finely crystalline yellow deposit was filtered out of it, washed with alcohol and with water, and dried; it weighed 1.0 g. Diluting the pyridine mother liquor with five times its volume of water yielded 0.25 g more of the same substance. The dimethylbiacridene was recrystallized from pyridine (1:200) for analytical purposes. The pyridine solution displayed extremely strong green fluorescence. The recrystallized N,N'-dimethyl-9,9'-biacridene consisted of bright-yellow, flat octagons with a m.p. of 354-355°.

7.216 mg substance: 0.4695 ml N_2 (22°, 730 mm); 3.287 mg substance: 10.481 mg CO_2; 1.728 mg H_2O. Found %: C 86.96; H 5.88; N 7.23. $C_{28}H_{22}N_2$. Computed %: C 87.01; H 5.74; N 7.24.

N,N'-Dimethyl-9,9'-biacridan. A mixture of 8.5 g of acridan methylbromide and 8.5 g of Raney's nickel paste in 300 ml of methanol was heated with constant stirring until the alcohol boiled gently for 2 hours. Toward the end of the reaction the brown color of the solution disappeared. The hot reaction solution was filtered, and the deposit of nickel and the reaction product was washed with

methanol and then boiled with 450 ml of pyridine. The nickel was filtered out of the hot solution. When the filtrate cooled down, crystals settled out. They were filtered out, washed carefully with methanol, and dried. This yielded 3.7 g of the substance. Dilution of the pyridine mother liquor with water yielded another 1.1 g of the substance. The yield was 4.8 g (80% of the theoretical). The substance was recrystallized from pyridine for analytical purposes; the resulting white needles of N,N'-dimethylbiacridan had a m.p. of 280-281°.

4.819 mg substance: 0.313 ml N_2 (18°, 727.5 mm). 4.244 mg substance: 13.492 mg CO_2: 2.890 mg H_2O. Found %: C 86.70; H 6.30; N 7.29. $C_{28}H_{24}N_2$. Computed %: C 86.56; H 6.22; N 7.21.

N,N'-dimethylbiacridan is insoluble or slightly soluble in ordinary organic solvents; it does not dissolve in dilute acids or alkalies (2.0N hydrochloric acid, or an alcoholic solution of KOH). It dissolves in concentrated sulfuric acid, forming a yellow solution. When 0.2 g of N,N'-dimethylbiacridan was heated with 6.0 ml of 2% nitric acid, we got a solution from which a precipitate was thrown down by neutralization with ammonia. Recrystallization of the precipitate from alcohol yielded 0.1 g of a substance with a m.p. of 200-201°, which was identical with a sample of N-methylacridone.

SUMMARY

1. In the chemiluminescent reaction of lucigenin, the intermediate product of its chemical transformations is a compound described in this paper for the first time: N,N'-dimethyl-9,9'-biacridene oxide.

2. The chemiluminescent reactions of N,N'-dimethyl-9,9'-biacridene and N,N'-dimethyl-9,9'-biacridene oxide are independent, though related, processes.

3. The conjectural ensuing conversion of N,N'-dimethyl-9,9'-biacridene oxide into N,N'-dimethyl-9,9'-biacridene oxide in a chemiluminescent reaction as the result of the action of hydrogen peroxide is unlikely.

4. The 9,9' bond in N,N'-dimethyl-9,9'-biacridene and N,N'-dimethyl-9,9'-biacridene oxide is highly stable. This refutes the supposition that the twinned acridine molecule breaks down during the chemiluminescent reaction, giving rise to N-methylacridone.

5. In the chemiluminescent reaction of N,N'-dimethyl-9,9'-biacridene or N,N'-dimethyl-9,9'-biacridene oxide with H_2O_2 in pyridine solution, only part of the molecules of the initial substance participates (as a catalyst) in the process of decomposing the H_2O_2 and emitting light.

6. The insolubility of N,N'-dimethyl-9,9'-biacridene oxide in water compels us to assume that those molecules of the intermediate oxide that participate in the chemiluminescent reaction of lucigenin in an aqueous medium are immediately converted by oxidation with hydrogen peroxide into a water-soluble compound, which may appear before the other N-oxides.

7. A new method is described for synthesizing lucigenin and its analogs, as well as a new method of synthesizing twinned acridines: biacridenes and biacridans.

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Fig. 3

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